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MASS FRAGMENTATION OF A RING-A AROMATIZED 6-AZASTEROID

(SHORT COMMUNICATION)

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Received August 5, 1980 In revised form February 27, 1981 Accepted for publication March 25, 1981**

Papers correlating the structures and mass spectra of lactams are known in the literature [1, 2]. The present communication is concerned with the mass spectral examination of 19-nor-6-aza-B-homocholesta-1,3,5(10)-trien-7-one (1) [3].

The mass spectrum of lactam 1 gave the molecular ion peak (1') at m/z381 (base peak), along with fragment ion peaks (2, 4, 5) due to the cleavage of rings C, D and the side chain [4]. Ion peaks (3, 6, 7, 8) are also obtained owing to carbonyl directed fragmentation [5, 6]. Modes a, b, c, d and e explain the genesis of these ions under electron impact.

Experimental

The mass spectrum was recorded on an AEIMS-9 mass spectrometer at 70 eV, using the direct insertion technique at a source temperature of about 250 °C. The mass composition and relative abundance of the fragment ions are given in Table I.

A									
Fragment ion	m/z	Composition	Abundance, %						
M+	381	$C_{26}H_{39}NO$	100						
$M^+-\mathrm{CH}_3$	366	$C_{24}H_{36}NO$	7.9						
M+-CO	353	$\rm C_{24}H_{39}N$	6.5						
2	226	$C_{14}H_{16}NO$	5.3						
3	184	$C_{13}H_{14}N$	9.1						
4	172	$C_{11}H_{10}NO$	7.9						
5	167	$C_{12}H_{23}$	50						
6	146	C ₉ H ₈ NO	15.7						
7	120	C_7H_6NO	17.1						
8	118	C_7H_4NO	28.9						

Table I

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SYNTHESIS AND CHARACTERIZATION OF COPPER(II) COMPLEXES OF CYCLOHEXANONE THIOSEMICARBAZONE

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Copper(II) complexes of the general composition $Cu(ligand)_2X_2$ (X = Cl⁻, Br⁻, NO₃⁻, ClO₄⁻, CH₃COO⁻ and 0.5 SO₄²⁻) have been synthesised with cyclohexanone thiosemicarbazone. Complexes are characterized by elemental analysis, magnetic moment, infrared, electronic and electron spin resonance spectral studies. Complex Cu(ligand)₂SO₄ is five-coordinate square pyramidal in geometry having $d_{X^2-y^2}$ ground state, the others are six-coordinate octahedral.

Introduction

Since DOMAGK's original discovery [1] of their antitubercular activity, thiosemicarbazones have been shown pharmacologically active against viruses, protozoa, small pox and certain kind of tumour [2]. It has been shown that the active species is not the thiosemicarbazone itself but a metal chelate of thiosemicarbazones [3].

In this paper we describe the preparation and characterization of Cu(II) complexes of cyclohexanone thiosemicarbazone (chtsc) (I).



All the complexes are of general composition: $Cu(chtsc)_2X_2$ (X = Cl⁻, Br⁻, NO₃⁻, ClO₄⁻ and 0.5 SO₄²⁻). Complexes are characterised by elemental analysis, magnetic moment, electronic, infrared and electron spin resonance spectral studies. $Cu(ligand)_2X_2$ (X = Cl⁻, Br⁻, NO₃⁻, ClO₄⁻ and CH₃COO⁻) are six-coordinate octahedral, while $Cu(ligand)_2SO_4$ is five-coordinate square pyramidal.

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Experimental

Preparation of cyclohexanone thiosemicarbazone

It is prepared by the method reported earlier [4].

Preparation of complexes

Hot aqueous ethanolic solutions of respective hydrated metal salt (0.05 mole) and the ligand (0.1 mole) were mixed in molar ratio 1:2. On cooling the complex separated in each case. It was filtered, washed with 50% ethanol and dried in an electric oven at \sim 60 °C.

Physical measurements

The metal content of the complexes, was determined as described earlier [4]. The microanalyses of carbon and hydrogen were performed in the departmental microanalytical laboratory. Nitrogen content was determined by KJELDAHL's method. Room temperature magnetic susceptibility measurements were made by the GOUY method using mercury(II) tetrathiocynatocobaltate(II) as a calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ cgs units). Electronic spectra were recorded on a Russian (CØ-10 automatic recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 437 spectrophotometer in KBr pellets. Esr measurements on the polycrystalline samples were carried out using a Varian E₄-EPR spectrometer operating at about 9.4 GHz with 100 KHz field modulation and phase sensitive detections.

Results and Discussion

All the complexes have composition $Cu(chtsc)_2X_2$, where $X = Cl^-$, Br^- , NO_3^- , CH_3COO^- , ClO_4^- and $0.5 SO_4^{2-}$ (Table I). Magnetic moments of all the complexes lie in the range 1.8-2.0 B. M. (Table II). Irrespective of the stereochemistry involved, bivalent copper(II) complexes contain one unpaired spin [5] per copper atom, unless there is antiferromagnetic exchange interaction between copper pairs, in which case lower magnetic moments or even diamagnetism result [19]. The data for the present complexes show absence of any such interaction [6].

en men en antiere en				C			
Complex	Colour	Analytical data, found (caled.)					
		% M	% C	% H	% N		
$Cu(chtsc)_2Cl_2$	Yellowish green	$13.58 \\ (13.32)$	35.50 (35 .2 5)	5.30 (5.45)	17.75 (17.62)		
$Cu(chtsc)_2Br_2$	Green	11.30 (11.27)	29.30 (29.81)	4.58 (4.61)	14.82 (14.90)		
${ m Cu(chtsc)_2(NO_3)_2}$	Yellowish green	12.12 (11.99)	31.50 (31.72)	4.95 (4.91)	21.25 (21.15)		
$Cu(chtsc)_2(ClO_4)_2$	Blue	10.60 (10.50)	_	_	13.70 (13.89)		
$Cu(chtsc)_2(CH_3COO)_2$	Blue	12.40 (12.12)	41.39 (41.26)	6.18 (6.11)	16.20 (16.04)		
$Cu(chtsc)_2SO_4$	Blue	13.00 (12.66)	33.67 (33.49)	5.25 (5.18)	16.97 (16.70)		

Table I

Colour and composition of the complexes

CHANDRA, SHARMA: COPPER(II) COMPLEXES

Carralan	Heff	Electronic spectra, transition assignment energy (cm-1)				
Complex	(B. M.)	${}^2B_{1g} \rightarrow {}^2A_{1g}$	${}^{2}B_{1g} \rightarrow {}^{2}B_{2g}$	${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$		
Cu(chtsc) ₂ Cl ₂	1.81	13 200	13 200-15 200	15 200		
Cu(chtsc) ₂ Br ₂	1.85	13 300	$13\ 300 - 15\ 500$	15 500		
$Cu(chtsc)_2(NO_3)_2$	1.95	13 500	13 500-15 700	15 700		
$Cu(chtsc)_2(ClO_4)_2$	1.81	13 600	13600 - 15700	15 700		
Cu(chtsc) ₂ (CH ₃ COO) ₂	2.01	14 000	14000 - 16600	16 600		
			${}^{2}B_{1} \rightarrow {}^{2}A_{1}$	Charge transfer		
Cu(chtsc) ₂ SO ₄	1.87	-	14 000	23 800		

Lable II	Т	ab	le	п
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Magnetic moments and electronic spectral bands ($\rm cm^{-1}$)

Magnetic moments of the complexes have also been studied at different temperatures.

		Т (К)							
Complex	373.2	343.2	303.2	264.7	186.1	109.1	80.4		
Cu(chtsc) ₂ Cl ₂	1.31	1.81	1.81	1.80	1.80	1.79	1.79		
Cu(chtsc) ₂ Br ₂	1.86	1.86	1.85	1.84	1.84	1.82	1.82		
Cu(chtsc ₂ (NO ₃) ₂	1.95	1.95	1.95	1.94	1.94	1.93	1.93		
Cu(chtsc) ₂ (ClO ₄) ₂	1.81	1.81	1.81	1.80	1.80	1.79	1.78		
Cu(chtsc) ₂ (CH ₃ COO) ₃	2.01	2.01	2.01	2.00	2.00	2.00	1.99		

The data show that the magnetic moment of the complexes do not depend on temperature.

 $Cu(chtsc)_2Cl_2$, $Cu(chtsc)_2Br_2$, $Cu(chtsc)_2(NO_3)_2$, $Cu(chtsc)_2(ClO_4)_2$ and $Cu(chtsc)_2(CH_3COO)_2$ may be considered to have tetragonal structure with planar arrangement of two chtsc molecules around copper(II) and the anions occupying *axial* positions. In the thiosemicarbazide (tsc) complex of copper(II) nitrate, $Cu(tsc)_2(NO_3)_2$, for which the crystal structure is known [7], the two tsc molecules are chelated in *trans*-configuration to give a near planar grouping, the six-coordination being completed by two oxygen atoms from the two *trans*-nitrate groups.

The absorption spectra of six-coordinate copper(II) complexes show D_4h or C_{4v} symmetry, the d_y and d_t levels of the 2D free ion term will further split into B_{1g} , A_{1g} and B_{2g} , E_g levels, respectively. Thus three spin allowed transitions are expected in the visible and near IR region, but only few complexes are known in which such bands are resolved either by Gaussian analysis or single crystal polarisation studies and are assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$

 $(d_z \rightarrow d_{x^2 \rightarrow y^2})$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ $(d_{xy} \rightarrow d_{x^2 \rightarrow y^2})$ and ${}^2B_{1g} \rightarrow {}^2E_g$ $(d_{xy}, d_{yz} \rightarrow d_{x^2 \rightarrow y^2})$ transitions in the order of increasing energy. The energy level sequence will depend on the amount of distortion due to ligand field and Jahn TELLER effect [9]. The electronic spectra of the complexes, Cu(ligand)₂X₂ (X = Cl⁻, Br⁻, NO₃⁻, ClO₄⁻ and CH₃COO⁻) display a sharp band in the range 15 200–16 950 cm⁻¹ and well-defined shoulder may be assigned to the ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, respectively. Because of the low intensity of ${}^2B_{1g} \rightarrow$ $\rightarrow {}^2B_{2g}$, this band is usually not observable as a separate band in the tetragonal field. The splitting of the 2E_g state is the measure of plane and axial fields and since the plane field is constant in all the present cases, the change of the position of the bands would be due to axial field only. In these copper(II) complexes ${}^2B_{2g} \rightarrow {}^2A_{1g}$ transition is shifted to higher energies in the order, Cl⁻ < Br⁻ < NO₃⁻ < ClO₄⁻ < CH₃COO⁻.

All the complexes show anisotropic esr spectra characteristic of tetragonal copper(II) complexes. g-Tensor values have been calculated by the KNEU-BUHL [10] method and the results are shown in Table III. The g values of copper(II) complexes are given by the following expressions [11-13].

$$egin{aligned} g_{||} &= 2 - rac{8\lambda}{arDelta E_2} \ g_{\perp} &= 2 - rac{2\lambda}{arDelta E_3} \end{aligned}$$

Stronger interaction along the z axis is to be accompanied by an increase in the $g_{||}$ value. Stronger *axial* bonding leads to an increase in the length of the bond in the xy plane, which results in a decrease of both in-plane covalency and the energy of $d_{x^2-y^2} \rightarrow d_{xy}$ transition [14]. Both of these effects are the factors, which tend to increase the value of $g_{||}$. The $g_{||}$ values for the complexes studied (Table III) follow the order, $Cu(chtsc)_2(NO_3)_2 > Cu(chtsc)_2Cl_2 > Cu(chtsc)_2(CH_3COO)_2$. Taking this to be the order of the strength of metal-anion interactions for chloride, nitrate and acetate, the result is in agreement with the respective position of the anions in the spectrochemical series [15]. A comparison of the g-tensor values of $Cu(chtsc)_2(NO_3)_2$, with those of $Cu(tsc)_2(NO_3)_2$ (table below) reveals the bonding in the two complexes to be of similar nature.

Complex	gx	g_y	g _z	Ref.
$ m Cu(chtsc)_2(NO_3)_2$	2.029	2.043	2.156	This work
$Cu(tsc)_2(NO_3)_2$	2.0269	2.0474	2.1525	[16]

Complex	g 11	g⊥	gav	k ₁₁	k_{\perp}	α	β	<i>β</i> 1	G	R
$Cu(chtsc)_2Cl_2$	2.133	$\begin{array}{c} 2.043 \\ 2.029 \end{array}$	2.068	$0.51 \! - \! 0.55$	0.49	$0.51\!-\!0.55$	0.89-0.97	1	3.69	-
Cu(chtsc) ₂ Br ₂	2.132	$\begin{array}{r} 2.040 \\ 2.026 \end{array}$	2.066	0.51 - 0.55	0.54	0.51 - 0.55	0.98-1.0	1	4.00	-
$Cu(chtsc)_2(NO_3)_2$	2.156	2.048 2.029	2.077	$0.56 \!-\! 0.60$	0.59	0.56 - 0.60	0.98-1.0	1	4.05	_
$Cu(chtsc)_2(ClO_4)_2$	2.138	$\begin{array}{r} 2.052 \\ 2.030 \end{array}$	2.073	0.49-0.53	0.61	0.49 - 0.53	$1.1\!-\!1.2$	1	3.68	-
Cu(chtsc) ₂ (CH ₂ COO) ₂	2.121	$2.082 \\ 2.041$	2.081	0.57-0.61	0.76	$0.57\!-\!0.61$	$1.2\!-\!1.3$	1	1.98	-
Cu(chtsc) ₂ SO ₄	2.158	$\begin{array}{c} 2.050\\ 2.029\end{array}$	2.079	_	-	-	_	-	-	0.185

Table III

Bonding coefficient parameters

The Schiff base [17] formation is expected to cause lowering in the electron density on the hydrazinic nitrogen and hence a lowering in its donor ability. This effect should lead to a comparatively stronger axial bonding as also reflected in the relative values of $g_{||}$ for the two complexes.

Further in an axial symmetry g values are related by the expression [9] $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, which measure the exchange interaction between copper centres in the polycrystalline solid. According [18-21] to HATHAWAY if the value of G is above four exchange interaction is negligible if, however, the value of G is less than four this indicates a considerable exchange interaction in the solid complexes. The calculated G values are given in Table III. G values for all the complexes studied follow the order, $Cu(chtsc)_2(CH_3COO)_2 < < Cu(chtsc)_2(NO_3)_2 < Ch(chtsc)_2Br_2 < Cu(chtsc)_2Cl_2$. This indicates that the acetato complex exhibits a lower G value and hence larger exchange interaction and the chloro complex exhibits higher G value and hence smaller exchange interaction.

The orbital reducation factors, K_{\parallel} and K_{\perp} which are the measure of the spin-orbit coupling constant $\lambda_0 = 823$ cm⁻¹ for free copper(II) ion in these copper(II) complexes are obtained using the expressions [22, 23]

$$egin{aligned} \mathbf{g}_z &= g_{||} \;= 2.0023 - 8K_{||}^2 \,\lambda_0 \,\big| \, \varDelta E(^2 B_{1g} o \,^2 B_{2g}) \ 0.5 \,(\mathbf{g}_{\mathbf{x}} + \mathbf{g}_{\mathbf{y}}) &= g_{\perp} = 2.0023 - 3K_{\perp}^2 \,\lambda_0 \,\big| \, \varDelta E(^2 B_{1g} o \,^2 E_g). \end{aligned}$$

The $K_{||}$ and K_{\perp} parameters (Table III) have been related variously as purely orbital coefficients and are related by $K_{||} = ca \cdot \alpha\beta$, and $K_{\perp} = ca \cdot \alpha\beta$, where α , β_1 and β are the coefficients of $d_{x^2-y^2}$, d_{xy} and d_{xz} , d_{yz} orbitals in the MO's to which they contribute; thus α measures σ -bonding, β_1 and β are in-plane π -bonding and out-of-plane π bonding coefficients respectively. By assuming $\beta_{|} = 1$ (since the ligand has no lone pairs available on the N atom for bonding with d_{xy}) the values of α and β are calculated for copper(II) complexes in this paper. The estimated α -coefficients suggest very little bonding of d_{xz} , d_{yz} with orbital of *axial* anions in these complexes.

 $Cu(chtsc)_2 SO_4$: Infrared spectrum of the complex under study shows six infrared bands due to the sulphate, indicating monodentate sulphate [24].

ν_1	ν_2	ν_{3}	ν_{4}
950 s	430 m	1020–1030 s 1120–1140 s	630 m

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A five-coordinate structure is thus readily suggested for this complex. There are two basic configurations [25] that can be adopted by complex compounds of coordination number five, the trigonal bipyramidal and the square pyramidal. In practice this appears to be a very little difference in energy [26] between the two configurations.

The two configurations, square pyramidal and trigonal bipyramidal, are characterized by the ground state $d_{x^2-y^2}$ and d_{z^2} , respectively [27, 28]. Esr spectra of copper(II) complexes provide a very good basis for distinguishing between these two ground states. For systems with $\mathbf{g}_3 > \mathbf{g}_2 > \mathbf{g}_1$ the ratio [29] of $(\mathbf{g}_2 - \mathbf{g}_1)/(\mathbf{g}_3 - \mathbf{g}_2)$ (hereafter called as parameter R) is a very useful parameter for this purpose. If the ground state is predominantly d_{z^2} the value of R is greater than one. On the other hand for the ground state predominantly $d_{x^2-y^2}$ the value [29] of R is less than one. For the complexes under study R is less than one indicating the $d_{x^2-v^2}$ ground state.

Thus for Cu(chtsc)₂SO₄, a five-coordinate square-pyramidal structure may be suggested in an, alogy with the corresponding thiosemicarbazide (tsc) complex, $Cu(chtsc)_2SO_4$ for which the molecular structure has been determined [30] by the single crystal method. The copper atom is five-coordinate; the tsc molecules are bonded in a *cis*-configuration, the two sulphur and two hydrazinic nitrogen atoms forming the corners of the base of a square-pyramid and the sulphato group. The Cu-O bond is relatively short (2.34 Å) showing that this bond is quite strong. A comparison (table below) of g values for $Cu(chtsc)_{2}SO_{4}$ and for six-coordinate tetragonal $Cu(chtsc)_{2}X_{2}$ complexes is interesting. Although the former is five-coordinate the axial Cu-O bond is apparently strong enough to overcome the total axial interactions from the two axial ligands in the six-coordinate tetragonal complexes.

Complex	gx	\mathbf{g}_y	\mathbf{g}_{z}	Ref.
$Cu(chtsc)_2SO_4$	2.050	2.050	2.158	This work
$Cu(chtsc)_2(NO_3)_2$	2.029	2.048	2.156	This work

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MAGNETIC AND SPECTRAL STUDIES OF SOME RARE EARTH CHELATES OF SUBSTITUTED THIOCARBAMIDES

(SHORT COMMUNICATION)

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Despite the considerable interest [1-9] in the sulphur ligated complexes, very little has been reported on rare earth metal ions [10-13]. This is probably due to the larger ionic radii of these metal ions and the lower electronegativity of the sulphur atom, which result in the formation of weak complexes. The present paper describes the isolation and characterization of rare earth metal complexes with N-benzoyl-N'-phenyl (BPTH₂), N-benzoyl-N'-orthochlorophenyl (BCPTH₂), N-benzoyl-N'-orthonitrophenyl (BNPTH₂), and N-benzoyl--N'-orthomethoxyphenyl (BMPTH₂) thiocarbamides.

Preparation of the Complexes

The complexes were prepared in aqueous ethanolic solution by mixing metal chloride and the appropriate ligand in 1:1 mole ratio. The pH of the vigorously stirred solution was adjusted by dropwise addition of a very dilute ammonium hydroxide ethanolic solution to just below that for hydrous hydroxide or oxideprecipitation over a period of 2 hours. The solution was then refluxed for 6-8 hours. The precipitate thus obtained was filtered, washed with water and ethanol, dried in vacuum over calcium chloride.

The elemental analyses and physical measurements were performed as described earlier [14].

Results and Discussion

The elemental analyses (Table I) indicate 1:1 metal to ligand stoichiometry for these complexes. The complexes are insoluble in all common organic solvents. The presence of coordinated water molecule in all these complexes has been confirmed by thermogravimetry.

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SENGUPTA: RARE EARTH CHELATES

Table I

Analytical and magnetic data of the complexes*

		Found (Caled.) %							
Complex	С	Ν	N	S	M	Cl	(300 °K)		
1	2	3	4	5	6	7	8		
$La(BPT)Cl \cdot H_2O$	37.3 (37.6)	2.4 (2.6)	6.0 (6.2)	6.8 (7.1)	31.0 (31.1)	7.6 (7.9)	Diamag.		
$La(BCPT)Cl \cdot H_2O$	34.6 (34.9)	2.0 (2.2)	5.5 (5.8)	6.4 (6.6)	28.6 (28.8)	14.5 (14.7)	Diamag.		
$La(BNPT)Cl \cdot H_2O$	34.0 (34.1)	1.9 (2.2)	8.2 (8.5)	6.1 (6.5)	28.0 (28.2)	7.0 (7.2)	Diamag.		
La(BMPT)Cl \cdot H ₂ O	37.4 (37.7)	2.5 (2.9)	5.5 (5.8)	6.4 (6.7)	29.0 (29.1)	7.1 (7.4)	Diamag.		
$Pr(BPT)Cl \cdot H_2O$	37.1 (37.5)	2.4 (2.6)	6.0 (6.2)	7.0 (7.1)	31.1 (31.2)	7.6 (7.9)	3.59		
$Pr(BCPT)Cl \cdot H_2O$	34.1 (34.8)	2.0 (2.2)	5.3 (5.8)	6.4 (6.6)	29.0 (29.0)	14.5 (14.7)	3.58		
$Pr(BNPT)Cl \cdot H_2O$	34.0 (34.1)	2.1 (2.2)	8.3 (8.5)	6.2 (6.4)	28.0 (28.4)	7.0 (7.2)	3.60		
$Pr(BMPT)Cl \cdot H_2O$	37.2 (37.6)	2.5 (2.9)	5.5 (5.8)	6.3 (6.7)	29.2 (29.3)	7.3 (7.4)	3.60		
$Nd(BPT)Cl \cdot H_2O$	37.0 (37.1)	2.2 (2.6)	6.0 (6.1)	6.7 (7.0)	31.4 (31.9)	7.6 (7.8)	3.49		
$Nd(BCPT)Cl \cdot H_2O$	34.4 (34.5)	2.2 (2.2)	5.5 (5.7)	6.4 (6.5)	29.6 (29.6)	14.6 (14.6)	3.50		
Nd(BNPT)Cl \cdot H ₂ O	33.4 (33.8)	2.1 (2.2)	8.1 (8.4)	6.2 (6.4)	28.7 (29.0)	6.9 (7.1)	3.50		
Nd(BMPT)Cl \cdot H ₂ O	37.1 (37.3)	2.6 (2.9)	5.7 (5.8)	6.4 (6.6)	29.5 (29.9)	7.0 (7.3)	3.50		
$Sm(BPT)Cl \cdot H_2O$	36.4 (36.6)	2.4 (2.6)	6.0 (6.1)	6.5 (6.9)	32.6 (32.8)	7.4 (7.7)	1.50		
$Sm(BCPT)Cl \cdot H_2O$	33.7 (34.0)	2.0 (2.2)	5.4 (5.6)	6.3 (6.4)	$30.2 \\ (30.5)$	14.3 (14.4)	1.48		
$Sm(BNPT)Cl \cdot H_2O$	33.1 (33.4)	2.0 (2.1)	8.0 (8.1)	6.0 (6.3)	29.5 (29.9)	6.7 (7.0)	1.50		
$Sm(BMPT)Cl \cdot H_2O$	36.4 (36.8)	2.7 (2.8)	5.6 (5.7)	6.2 (6.5)	30.5 (30.8)	7.0 (7.2)	1.49		
Gd(BPT)Cl · H ₂ O	36.0 (36.1)	2.2 (2.5)	6.0 (6.0)	6.4 (6.8)	33.5 (33.8)	7.5 (7.6)	7.87		
$Gd(BCPT)Cl \cdot H_2O$	33.4 (33.6)	2.0 (2.2)	5.3 (5.6)	6.1 (6.4)	31.0 (31.4)	14.0 (14.2)	7.85		
$Gd(BNPT)Cl \cdot H_2O$	32.8 (32.9)	2.1 (2.1)	8.0 (8.2)	6.1 (6.2)	30.6 (30.8)	6.9 (6.9)	7.84		
$Gd(BMPT)Cl \cdot H_2O$	36.0 (36.3)	2.5 (2.8)	5.2 (5.6)	6.3 (6.4)	31.5 (31.7)	7.1 (7.1)	7.87		

* where $BPTH_2 = C_{14}H_{12}N_2SO$, $BCPTH_2 = C_{14}H_{11}N_2SOCI$, $BNPTH_2 = C_{14}H_{11}N_2SO.NO_2$, $BMPTH_2 = C_{14}H_{11}N_2SO$ OCH_3 .

Magnetic moments and electronic spectra

The values of the magnetic moments and electronic spectral data are given in Tables I and II. The magnetic moments of the complexes measured at room temperature show little deviation from VAN VLECK values [15] indicating that the 4f electrons do not participate in bond formation. Since electrons in the 4f orbitals are well shielded from the ligand by the intervening $5s^25p^6$ octet, the order of perturbations for a lanthanide ion is: crystal field spin orbit coupling interelectronic repulsions. Thus the line like absorption spectra appearing in the spectra of complexes arise from electronic transitions within the 4f levels. Thus the absorption bands of praseodymium(III), neodymium(III), samarium(III), and gadolinium(III) appear due to the transitions [16] from the ground levels ${}^{3}H_{4}$, ${}^{4}I_{9/2}$, ${}^{8}G_{7/2}$ to the excited J levels of 4f configuration, respectively.

Infrared spectra

The electronic spectra of the ligands show one band at $ca. 36\ 000-35\ 000$ cm⁻¹ which is characteristic of a conjugated compound and provide evidence in favour of the structural form **A**.



 $(X = H, Cl, OMe, NO_2)$

The bands appearing at ca. $3400-3200 \text{ cm}^{-1}$ and $2460-2440 \text{ cm}^{-1}$ due to v(OH) and v(SH) vibrations [17] in the IR spectra of the ligands disappear in the complexes. The coordinations through phenolic oxygen and thiolo sulphur have further been confirmed by the appearance of new bands at ca. 540-500 and $390-340 \text{ cm}^{-1}$ in the spectra of complexes assignable [18] to v(M-O) and v(M-S) vibrations, respectively. The ligands also show one broad band at ca. $1620-1610 \text{ cm}^{-1}$ which may be assigned [19] to v(C=N). In the complexes this band shifts to lower frequency $\sim(30-25 \text{ cm}^{-1})$ indicating the coordination of the azomethine nitrogen to the metal atom. The bands due to v(M-N) appear [18] at ca. $450-420 \text{ cm}^{-1}$.

Thus, on the basis of above discussion, it can be concluded that each ligand has four potential coordinating sites; two azomethine nitrogen, one sulphur atom and one phenolic oxygen atom. The possibility of coordination by both the nitrogen atoms of the azine group to the same metal atom is unlikely. Coordination of these two nitrogen atoms to two different metal

Table II

Electronic spectral bands (cm⁻¹) of the complexes

Complex	Bands	Assignments	Complex	Bands	Assignments
1	2	3	4	5	6
Pr(BPT)Cl.H ₂ O	5 300 5 990 6 500 16 500 20 000 24 800 35 200	${}^{3}H_{4} \rightarrow {}^{3}F_{2}$ $\rightarrow {}^{3}F_{3}$ $\rightarrow {}^{1}G_{4}$ $\rightarrow {}^{1}D_{2}$ $\rightarrow {}^{3}P_{2}$ Internal ligand transition	Nd(BPT)Cl.H ₂ O	11 400 12 200 12 600 13 200 13 600 17 000 18 900 19 200 20 500 23 000 36 000	$\begin{array}{cccc} {}^{4}I_{9/2} \rightarrow {}^{4}H_{3/2} \\ \rightarrow {}^{4}F_{5/2} \\ \rightarrow {}^{2}H_{9/2} \\ \rightarrow {}^{4}F_{7/2} \\ \rightarrow {}^{2}S_{3/2} \\ \rightarrow {}^{4}G_{5/2} \\ \rightarrow {}^{4}G_{7/2} \\ \end{array}$ $\begin{array}{c} \rightarrow {}^{2}G_{9/2} \\ \rightarrow {}^{2}G_{9/2} \\ \rightarrow {}^{2}P_{1/2} \\ \end{array}$ Internal ligand transition
Pr(BCPT)Cl.H ₂ O	$\begin{array}{c} 5 \ 150 \\ 6 \ 000 \\ 6 \ 400 \\ 17 \ 000 \\ 20 \ 800 \\ 23 \ 900 \\ 35 \ 800 \end{array}$	-do-	Nd(BCPT)Cl.H ₂ O	11 200 12 000 12 500 13 000 17 200 18 000 19 100 21 000 23 200 35 800	-do-
Pr(BNPT)Cl.H ₂ O	$\begin{array}{c} 5 \ 380 \\ 6 \ 010 \\ 6 \ 480 \\ 16 \ 800 \\ 21 \ 000 \\ 24 \ 000 \\ 35 \ 000 \end{array}$	-do-	Nd(BNPT)Cl.H ₂ O	11 500 12 100 12 200 13 200 17 000 18 100 19 000	-do-
Pr(BMPT)Cl.H ₂ O	$\begin{array}{c} 5 \ 200 \\ 6 \ 000 \\ 64 \ 500 \\ 17 \ 000 \\ 20 \ 200 \\ 24 \ 200 \\ 36 \ 000 \end{array}$	-do-		$\begin{array}{c} 21 \ 200 \\ 23 \ 000 \\ 35 \ 500 \end{array}$	
Sm(BPT)Cl.H ₂ O	8 200 9 300 17 500 18 800 200 000 20 500 21 500 23 000 24 500 25 000 36 000	$ {}^{6}H_{5/2} \rightarrow {}^{6}F_{7/2} \\ \rightarrow {}^{4}F_{9/2} \\ \rightarrow {}^{4}G_{5/2} \\ \rightarrow {}^{4}G_{7/2} \\ \rightarrow {}^{4}G_{7/2} \\ \rightarrow {}^{4}G_{7/2} \\ \rightarrow {}^{4}I_{13/2} \\ \rightarrow {}^{6}P_{5/2} \\ \rightarrow {}^{6}P_{3/2} \\ \rightarrow {}^{4}F_{9/2} \\ \end{array} $ Internal ligand transition	Nd(BMPT)Cl.H ₂ O	11 700 12 000 12 800 13 500 13 700 17 100 18 000 19 200 21 000 23 200 36 000	-dc

Table II (Continued)

Complex	Bands	Assignments	Complex	Bands	Assignments
1	2	3	4	5	6
Sm(BCPT)Cl.	8 100		Gd(BPT)Cl.H.O	31 000	$8S_{\pi/2} \rightarrow {}^6P_{\pi/2}$
$.\mathrm{H}_{2}\mathrm{O}$	9 000			35 200	Internal ligand
	17 000				
	18 500			36 400	$\rightarrow {}^{6}I_{9/2}$
	20 200			37 000	$\rightarrow {}^{6}I_{15/2}$
	21 300			40 200	$\rightarrow {}^6D_{5/2}$
	23 200				
	24 200				
	25 100				
	35 800			-	
Sm(BNPT)Cl.	8 000		Gd(BCPT)Cl.H ₂ O	31 200	-do-
$.H_2O$	9 100			35 800	
	17 200			37 500	
	18 300	-do-	Gd(BMPT)Cl.H ₂ O	31 850	
	$20\ 100$			35 500	
	20 500			36 370	-do-
	21 000			37 250	
	22 800			40 900	
	24 000				
	•25 000				
	35 000				
Sm(BMPT)Cl.	8 300				
$.H_2O$	9 000				
	$17\ 000$				
	18 100				
	20 000		-do-		
	20 400				
	21 000				
	22 000				
	24 200				
	25 100				
	35 300				1

atoms are possible in which the -OH and -SH groups should be trans with respect to the C=N-C=N skeleton and each of them combine with two different metal atoms; if the two groups are in cis position and attached to the same metal atom, it will involve a strained ring. Then insolubility of the complexes in all common organic solvents can also be explained by the existence of a polymeric structure.

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TRANSITION METAL COMPLEXES OF DIBASIC TRIDENTATES WITH OXYGEN AND NITROGEN COORDINATING SITES

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Two novel dibasic tridentates have been synthesised by the condensation of pyrrole-2-carboxaldehyde with β -amino acids. Complexes of the tridentates with Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been isolated. The newly synthesized molecular adducts of 1 : 1 stoichiometry have been characterized through elemental analysis, molecular mass, conductance, potentiometric, magnetic and spectroscopic data. Various spectroscopic parameters, viz. 10 Dq, B, v_2/v_1 and λ , for these complexes have also been evaluated. The IR studies reveal that the ligand coordinates through pyrrole nitrogen, azomethine nitrogen and the sulphonate group besides three water molecules to form a chelate, displaying octahedral stereochemistry. It is expected that the two ligands are structurally similar and behave as dibasic tridentates.

Introduction

Earlier we have reported [1-3] on complexes of various transition metals with a view to study their thermodynamic and electrometric significance. In the present paper we report on transition metal complexes of dibasic tridentates with oxygen and nitrogen donor atoms. Their spectroscopic, magnetic, conductance and potentiometric studies were carried out and structures established.

Materials and Methods

O- $(N-\alpha$ -pyrrolideneimino)benzene sulphonic acid (H₂PB) and 2- $(N-\alpha$ -pyrrolideneimino) ethane sulphonic acid (H₂PE) were synthesized by the condensation of pyrrole-2-carboxaldehyde with orthanilic acid and taurine, respectively, by the method already reported previously [4].

Orthanilic acid contains a phenyl ring while taurine contains an open chain molecule. The authenticity of the compounds were established on the basis of elemental analysis molecular mass and IR spectra [H₂PB, m.p. 172 °C and H₂PE, m.p. 210 °C]. The metal nitrates (BDH) and other solvents were reagent grade chemicals.

The following general procedure was used for the isolation of Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes. H_2PB or H_2PE (0.005 mole) was dissolved in 40-60 mL of 80% ethanol. A solution of metal nitrates (0.005 mole) in 10-20 mL of 80% ethanol was

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treated exactly in the same manner. Ligand and metal nitrate solutions were mixed and refluxed in nitrogen atmosphere to prevent the oxidation of metal ion, on a steam-bath for 3-4 hrs. Crystalline solid was obtained which was filtered, washed with ethanol and recrystallised.

The C, H, N and S were determined microanalytically and the metal content in the complexes were estimated [5] by EDTA titration using Eriochrome Black T as an indicator after destroying the organic part first with aqua regia and then with concentrated H_2SO_4 .

Conductance measurements were made on a Toshniwal conductivity bridge. A digital pH-meter, type DPH-77 (Unitec) equipped with a glass-calomel electrode assembly was used to determine the pH. The potentiometric studies were carried out by the CALVIN-BJERRUM titration technique [6] at 35 °C in aqueous media ($\mu = 0.1 M$ NaClO₄). Molecular masses were determined ebulliometrically in dioxan. Magnetic measurements at room temperature were made on a GOUY magnetic balance using Hg[Co(NCS)₄] as a calibrant, diamagnetic corrections were applied using PASCAL'S constants [7]

A VEB Carl-Zeiss, Jena, VSU-2P spectrophotometer was used to record the electronic spectra. The IR spectra in Nujol were recorded on a Perkin-Elmer spectrophotometer using NaCl prism.

Results and Discussion

The pK₁ and pK₂ of H₂PB and H₂PE were determined potentiometrically. The values are: 3.00, 10.00, and 7.50, 9.00, respectively, at 35 °C ($\mu = 0.1 \ M \ NaClO_4$). These values suggest the biprotic nature of the ligands which are completely deprotonated. The formation curves of the ligands (H₂PB and H₂PE) are shown in Fig. 1. The pK₁ and pK₂ values correspond to the liberation of protons of the sulphonic (-SO₃H) and imino (-NH) groups,



Fig. 1. Formation curves of H,PB and H,PE at 35 °C

Ligand/ Metal Complex	$pK_1/log K_1$	$pK_2/\log K_2$
H_2PB	3.00	10.00
H_2PE	7.50	9.00
Cr(II)	3.90 (7.85)	2.60 (5.10)
Mn(II)	4.15 (8.40)	2.75 (5.65)
Fe(II)	4.70 (8.75)	3.00 (6.05)
Co(II)	5.20 (9.40)	3.35 (6.60)
Ni(II)	6.25 (10.20)	4.25 (7.05)
Cu(II)	7.20 (10.60)	5.40 (7.90)

Dissociation constants of H_2PB and H_2PE^* and stability constants of their transition metal complexes at 35 °C ($\mu = 0.1 M \text{ NaClO}_4$)

Table I

* Values in parenthesis for H₂PE complexes

respectively. The stability constants (Table I) of Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)-complexes of H₂PB and H₂PE suggest the formation of 1:1 (metal-ligand) complexes. The stability order Cr(II) < Mn(II) < Fe(II) < < Co(II) < Ni(II) < Cu(II) is in agreement with IRVING-WILLIAM's rule [8].

In order to ascertain the number of water molecules present in the complexes, these materials were subjected to thermogravimetric analyses. In all cases it revealed a weight-loss equivalent to three water molecules. It means that each metal ion in its complexes molecule is coordinated to three water molecules.

The solid complexes were analyzed and their molecular mass determined (Table II). 1:1 metal to ligand stoichometry was found.

On the basis of elemental analyses, molecular mass and thermogravimetric data, the composition of the metal complexes may be expressed as $[MLX_3]$ or $[ML'X_3]$ where M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II); $LH_2 = (C_{11}H_{10}N_2SO_3)$ or $L'H_2 = (C_7H_{10}N_2SO_3)$ and $X = H_2O$. Thus the deprotonated forms of the ligands and 1 : 1 (metal to ligand) stoichiometry of the complexes are also evident from the potentiometric studies (Table I).

The molar conductances in MeOH $(10^{-3} M \text{ solution})$ are in the ranges $3.8-10.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ suggesting that the complexes are nonionic in nature [9]

These compounds do not possess sharp m.p., but when heated between 290 and 340°, they decompose to give their metal oxides.

Table II

C	Mol. mass		⊿ _M Ohm-		
Compound	Found (Calcd.)	N	S.	Metal	cm ² mole-
[CrLX ₃]	342 (355)	7.80 (7.89)	8.93 (9.01)	14.49 (14.65)	5.6
[MnLX ₃]	348 (357)	7.81 (7.84)	8.84 (8.96)	15.20 (15.40)	6.7
[FeLX ₃]	348 (358)	7.80 (7.82)	8.80 (8.93)	15.46 (15.66)	4.2
[CoLX ₃]	350 (362)	7.70 (7.75)	8.72 (8.86)	16.21 (16.34)	9.5
[NiLX ₃]	351 (361)	7.73 (7.76)	8.73 (8.87)	16.16 (16.25)	8.3
[CuLX ₃]	355 (369)	7.61 (7.66)	8.64 (8.75)	17.19 (17.36)	7.1
[CrL'X ₃]	295 (306)	9.07 (9.15)	10.38 (10.46)	16.86 (16.99)	3.8
[MnL'X ₃]	296 (309)	8.94 (9.06)	10.21 (10.35)	17.60 (17.77)	8.0
$[FeL'X_3]$	297 (310)	8.93 (9.03)	$10.20 \\ (10.31)$	17.90 (18.02)	6.5
$[CoL'X_3]$	300 (313)	8.09 (8.94)	10.14 (10.22)	18.62 (18.82)	10.0
[NiL'X ₃]	302 (313)	8.90 (9.95)	10.15 (10.23)	18.58 (18.75)	10.2
[CuL'X ₃]	306 (318)	8.75 (8.81)	9.96 (10.08)	19.78 (19.98)	9.3

Molecular mass, elemental analyses and conductance data of transition metal complexes of H₂PB and H₂PE

 $LH_2 = (C_{11}H_{10}N_2SO_3)$ and $L'H = (C_7H_{10}N_2SO_3)$

The magnetic moments of Cr(II) complexes lie between 4.81 and 4.85 B. M. at room temperature which are higher than those reported [10] for high spin six-coordinated Cr(II) complexes.

Since high-spin Mn(II) complexes have an orbitally non-degenerate ⁶S ground term, the spin-only magnetic moment of 5.92 B. M. is expected which will be independent of the temperature and stereochemistry. The present complexes show $\mu_{\rm eff}$ values in the range 5.82–5.86 B. M. at room temperature which are consistent with the high-spin nature of the complexes and presence of five unpaired electrons in octahedral environment. The Fe(II) complexes display magnetic moment in the range 5.42–5.49 B. M. suggesting the octahedral geometry for these complexes.

The μ_{eff} value of Co(II) complexes lie between 4.84-5.70 B. M., which are higher than the spin-only value. These can be explained on the basis of O_h symmetry involving a high degree of orbital contribution due to the three-

fold orbital degeneracy of the ${}^{4}T_{1g}$ ground state. It is not surprising that the ligands in the equitorial position being less hindered, favour on O_{h} symmetry [11]. The magnetic moment values of Ni(II) complexes are in the range 3.15-3.35 B. M. in conformity with the high-spin configuration of octahedral Ni(II) complexes. The observed μ_{eff} values (1.82–1.85 B. M.) or Cu(II) complexes are very close to the spin-only value (1.73 B. M.) for one unpaired electron. It supports a distorted octahedral geometry in terms of JAHN-TELLER effect [12].

Electronic Spectra

The electronic spectra typical for octahedral coordination, observed for Cr(II) complexes, correspond to the transition ${}^{5}E_{g} \rightarrow {}^{5}T_{2g}$.

The spectra of Mn(II) complexes, which correspond to the transitions ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$ and ${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}(G)$ viz v_{1}, v_{2} and v_{3} , respectively, are characteristic of octahedral geometry around the metal ion.

A band observed in the spectrum of Fe(II) complexes may be attributed to the transition ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}(D)$ which suggests nearly octahedral stereochemistry of Fe(II) complexes.

The electronic spectra of Co(II) complexes give three distinct transitions ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, v_1 ; ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$, v_2 and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(P)$, v_3 . These bands are typical for high-spin octahedral Co(II) complexes. The splitting of v_3 band into two or more compounds in Co(II) complexes, may be due to lifting of degeneracy of ${}^{4}T_{1g}$ level either by the spin-orbital coupling or by the presence of a low symmetry component in the ligand field. However, the v_2/v_1 , ratio (1.75-1.95) and chocolate red colour of these complexes support an octahedral geometry.

Spectra of all Ni(II) complexes are typical of octahedrally [10] coordinated Ni(II) in as much as they exhibit three d-d traditions bands viz. ${}^{3}A_{2g} \rightarrow {}^{4}T_{2g}(F)$, ${}^{3}A_{2g} \rightarrow {}^{1}E_{g}(D)$ and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ corresponding to v_{1} , v_{2} and v_{3} bands. The yellowish-green colour of the triaqua complexes also supports the O_{h} symmetry. These spectral data are utilized to compute the important ligand field parameters 10 Dq, B and λ using the ligand field theory of spinallowed transitions in d^{8} -configuration. Comparison of 10 Dq and B values for the complexes indicates, that the ligands give rise to reasonably strong ligand fields and lead to reasonably strong covalent bonds. The high values of 10 Dq and B are consistent with the nitrogen coordination of the azomethine group [13]. The ratio of v_{2}/v_{1} lies between 1.91 and 1.93 as expected for octahedral Ni(II) complexes.

The spectra of Cu(II) complexes correspond to the transitions ${}^{2}B_{1} \rightarrow {}^{2}A_{1g}$, ${}^{2}B_{1} \rightarrow {}^{2}E_{g}$ and $C \rightarrow T$ (charge-transfer band) viz. v_{1} , v_{2} and v_{3} and these bands are quite intense with ε of the order of $10^{2}-10^{3}$. The broadness of the bands and their position indicate tetragonally distorted octahedral symmetry for

these complexes. JORGENSEN [14] has used the ratio $v_{\rm Cu}/v_{\rm Ni}$ between the wave number of the principal band of Cu(II) complex and the wave number of first spin-allowed band of the high-spin octahedral Ni(II) complex, with the same ligand, as a measure of tetragonality of the Cu(II) complexes. The ratio $v_{\rm Cu}/v_{\rm Ni}$ forH₂PB and H₂PE are found to be 1.24 and 1.31, respectively, indicating that [Cu(PE)X₃] complex is more tetragonally distorted than [Cu(PB)X₃] complex. The latter also shows a shoulder on the low energy side, this may be due to transition from d_{z^2} , the σ antibonding from the weakly bound ligands on z-axis, to the hole in $d_{x^2-y^2}$.

I. R. Spectra

In the i.r. spectra of H_2PB or H_2PE three bands were observed in the ranges $3200-3240 \text{ cm}^{-1}$, $1160-1180 \text{ cm}^{-1}$ and $1610-1630 \text{ cm}^{-1}$ assignable to bonded vNH, $v_{as}(SO_3H)$ and vC=N, respectively. It appears that imine nitrogen is hydrogen bonded to the lone pair of the azomethine nitrogen atom. The absence of vNH in the spectra of metal complexes indicates the rupture of hydrogen bond and involvement of the imine nitrogen in complexation. The band in the range $1160-1180 \text{ cm}^{-1}$ also disappeared suggesting coordination through the sulphonate group. vC=N of H_2PB or H_2PE around $1610-1630 \text{ cm}^{-1}$ was shifted to the lower frequency side on complexation suggesting the participation of azomethine nitrogen in coordination. The appearance of two new bands in the regions $530-560 \text{ cm}^{-1}$ and $410-450 \text{ cm}^{-1}$ in metal complexes suggest M-O and M-N bondings [15] in them, respectively. All the complexes give one broad band in the region $3450-3470 \text{ cm}^{-1}$ due to vOH of water molecule present.

Compound	ν_1	v_2	v_{2}	10 Dq (cm ⁻¹)	$B \pmod{(\operatorname{cm}^{-1})}$	v_2/v_1	10 Dq/B	λ (cm ⁻¹)
Cr(II)	16 550			-	-	_		-
	(16 240)					-		
Mn(II)	20 430 (20 100)	23 700 (23 600)	26 240 (26 450)	3300 (2500)	756.6 (683.3)	$1.168 \\ (1.174)$	4.36 (5.12)	618 (527)
Fe(II)	10 960 (11 100)	_	_	_	_	_	_	-
Co(II)	9 870 (8 960)	$17 340 \\ (17 520)$	$21 470 \\ (21 310)$	7470 (8560)	613.3 (796.6)	1.756 (1.955)	12.18 (10.74)	216 (251)
Ni(II)	9 350 (9 290)	17 860 (17 970)	25 980 (25 790)	8510 (8680)	1052.6 (1059.2)	1.910 (1.934)	8.08 (8.19)	312 (329)
Cu(II)	11 660 (11 780)	15 150 (15 460)	23 830 (23 800)	3550 (3880)	266.6 (261.3)	1.306 (1.312)	12.74 (14.84)	211 (181)

 Table III

 Electronic transition (in cm⁻¹) and relevant spectroscopic parameters of transition metal complexes of H₂PB and H₂PE*

* Values in parenthesis for H₂PE complexes

The results obtained conclusively indicate that the general similarity of the complexes of H₂PB and H₂PE are not due to the presence or absence of an open chain or a phenyl ring but it is only due to the presence of nitrogen atom of azomethine group in β -position to the sulphonic group which is in agreement with the findings of KISHITA et al. [16].

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STUDIES ON THE CHELATES OF 2-(2-HYDROXYPHENYL) HYDRAZONOPENTANE, 2,4-DIONE (H.P.P.D.)

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In view of the medicinal importance of 2-(2-hydroxyphenyl) hydrazonopentane--2,4-dione (HPPD),the coordination behaviour has been studied by physico-chemical methods. The 1:1 and 1:2 (M:L) chelates with Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) have been isolated and characterised on the basis of chemical analysis, molar conductance, magnetic moment, I.R. studies and electronic spectra. The ligand behaved as a tridentate one except in Cu(II) 1:2 chelate where it behaved as bidentate. Fe(II), Ni(II), Co(II) and Mn(II) chelates are high spin octahedral while Cu(II) chelates are square planar.

Introduction

Hydrazones are of importance as they find use in organic syntheses [1-3] detection of metal ions [4] and because of their high physiological activity [5]. They find use [4] as herbicides, insecticides, antimicrobial agents, antioxidants and have been claimed effective against leprosy, leukaemia and other malignant neoplasm. F. LIONS [6] has studied metal complexes with first row transition metals, EVANS et al. [7] have studied copper chelates of substituted hydrazones. Further BALKRISHNAN et al. [8] have used hydrazones for synthesizing metal templates. Keeping in view the importance of hydrazones we have reported polarographic reduction and coordination behaviour of few hydrazones [9-11]. Here we report on the physico-chemical studies on some 1:1 and 1:2 (M:L) metal chelates of 2-(2-hydroxyphenyl)-hydrazonopentane-2,4-dione (HPPD), which has been used as an intermediate [12] for the synthesis of a number of potential antidiabetic and antineoplastic compounds, with Cu(II), Ni(II), Cd(II), Fe(II) and Mn(II).

Experimental

Reagent and materials

Nickel, cobalt, copper nitrates, manganese acetate and ferrous ammonium sulphate used were of G.R. grade. The ligand was synthesised according to the literature procedure [12].

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Synthesis of the chelates

The methanolic solution (0.005 mol) of the ligand and metal salt solution (0.005 mol) in methanol were mixed in ratio 1:1 and 1:2 (M:L). In case of ferrous ammonium sulphate it was first dissolved in perchloric acid and then methanol was added, the water content in the solution was 20% (v/v). The contents were refluxed for about two and half hours. Most of the chelates got precipitated on cooling, while others got precipitated when about half of the solvent was **removed** by distillation. The precipitates were filtered, washed and dried in vacuum over anhyd. CaCl₂.

Apparatus and procedure

Chemical analysis was done at I.I.P. Dehradun. The conductance of chelates was measured in dimethylformamide on Systronic type 302 conductivity bridge using a dip type cell. The magnetic moment was determined by a Guoy balance at room temperature, $24^{\circ} \pm 0.2^{\circ}$ C. I.R. spectra of the ligand and the chelates were recorded on a Beckmann I.R. 20 Spectrophotometer in KBr disc. Methanolic solution of the chelates was used for recording electronic spectra on Unicam SP 8000 spectrophotometer.

Results and Discussion

The ligand, HPPD has the following structure, and it is seen from the molecular formulas assigned to chelates on the basis of analytical results that



it forms both 1:1 and 1:2 chelates. The molar conductance data [13] also support the formulae (Table I) assigned to these chelates. However, molar conductance of 1:1 copper chelate was unusually low as compared to others. The non electrolyte behaviour of copper chelates suggest that both the protons, of hydroxyl and hydrazone group are released on coordination. This observation finds support in subsequent IR studies. The magnetic moment values indicate the presence of 5, 4, 3, 2 and 1 unpaired electrons in the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) chelates, respectively. The magnetic moment values suggest that all the chelates except of copper have high spin octahedral geometry, while the copper chelates may have either square planar or tetrahedral geometry.

Electronic spectra

The bands observed are recorded in Table II. The two high intense bands in the region 39 000-41 000 cm⁻¹ and 34 000-36 000 cm⁻¹ can be assigned to $\pi \to \pi^*$ transition of phenolic and azomethine groups [14]. The bands

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S. No.	Chelates	C% Calculated (found)	H% Calculated (found)	N% Calculated (found)	Molar conduc- tance ohm ⁻¹ cm ² mol ⁻¹	$^{\mu_{eff}}_{\mathrm{B.M.}}$
1.	$[Mn(C_{11}H_{11}N_2O_3)(CH_3OH)_3]CH_3OO$	44.76 (44.52)	6.06 (6.12)	6.56 (6.32)	72	5.92
2.	$[{\rm Fe}({\rm C}_{11}{\rm H}_{11}{\rm N}_2{\rm O}_3)({\rm H}_2{\rm O})_3]{\rm ClO}_4$	30.91 (30.85)	3.98 (4.03)	6.56 (6.34)	87	5.32
3.	$[{\rm Co}({\rm C}_{11}{\rm H}_{11}{\rm N}_{2}{\rm O}_{3})({\rm CH}_{3}{\rm O}{\rm H})_{3}]{\rm NO}_{3}$	38.62 (38.71)	5.29 (5.22)	9.66 (9.51)	92	5.12
4.	$[\rm{Ni}(\rm{C}_{11}\rm{H}_{11}\rm{N}_{2}\rm{O}_{3})(\rm{CH}_{3}\rm{OH})_{3}]\rm{NO}_{3}$	38.64 (38.39)	5.29 (5.40)	9.67 (9.54)	90	3.12
5.	$[{\rm Cu}({\rm C}_{11}{\rm H}_{10}{\rm N}_{2}{\rm O}_{3}){\rm CH}_{3}{\rm OH}]$	46.0 1 (46.12)	4.47 (4.62)	8.95 (8.91)	4	1.79
6.	$[\mathrm{Mn}(\mathrm{C}_{11}\mathrm{H}_{11}\mathrm{N}_{2}\mathrm{O}_{3})_{2}]$	53.55 (53.42)	4.46 (4.37)	11.36 (11.12)	7	5.96
7.	$[{\rm Fe}(C_{11}{\rm H}_{11}{\rm N_2O_3})_2]$	53.44 (53.12)	4.45 (4.57)	11.34 (11.09)	3	5.45
8.	$[{\rm Co}({\rm C}_{11}{\rm H}_{11}{\rm N}_{2}{\rm O}_{3})_{2}]$	53.23 (53.14)	4.44 (4.61)	11.29 (11.13)	9	5.22
9.	$[\rm{Ni}(\rm{C}_{11}\rm{H}_{11}\rm{N}_{2}\rm{O}_{3})_{2}]$	55.25 (55.02)	4.44 (4.53)	$11.30 \\ (11.22)$	11	3.21
10.	$[\mathrm{Cu}(\mathrm{C}_{11}\mathrm{H}_{11}\mathrm{N}_{2}\mathrm{O}_{3})_{2}]$	52.69 (52.57)	4.39 (4.51)	11.18 (11.02)	4	1.82

Analytical, molar conductance and magnetic data of metal - HPPD chelates

below 25 000 cm⁻¹ and relatively much weaker in intensity are assigned to d-d transitions [15]. However, where the metal is easily oxidisable and the ligand reducible, charge transfer band on low energy side may be obtained [16]. Thus in view of the easily reducible nature of the ligand, the two intense bands obtained in the region 16 000-23 800 cm⁻¹ for Fe(II) chelates appear to be due to metal to ligand charge transfer process [16].

The electronic spectra of nickel chelates (Table II) show major bands at 15 000-14 000 and 8000-8400 cm⁻¹ and may be assigned to ${}^{3}A_{2g(F)} \rightarrow$ $\rightarrow {}^{3}T_{1g(F)}(v^{2}); {}^{3}A_{2g(F)} \rightarrow {}^{3}T_{2g(F)}(v_{1})$. The third band $(v_{3}) {}^{3}A_{2g(F)} \rightarrow {}^{3}T_{1g(P)}$ could not be observed as the band due to -NH-N=C band masked it, but later it was calculated by the method of LEVER [17]. v_{2} transition has shoulder indicating that octahedral geometry is slightly distorted obviously due to the non identical nature of the donor atoms [18]. The v_{2}/v_{1} ratio is 1.61, a value usually accepted for octahedral nickel(II) chelates.

The electronic spectra of cobalt(II) chelates show bands at 8540-9000 cm⁻¹ ${}^{4}T_{1g} \rightarrow {}^{4}T_{2g}$ (v_1) , at $18\ 400-19\ 500$ cm⁻¹ ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}$ (v_2) and a band at $20\ 400-22\ 800$ cm⁻¹ ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g(P)}$ (v_3) indicating octahedral geometry

Assignment of the electronic spectral bands of HPPD chelates							
Chelate	$\pi - \pi^*$ (Phenolic), cm ⁻¹	$\pi - \pi^*$ (C=N), cm ⁻¹	d—d transitions, cm ⁻¹				
[Ni(HPPD)(CH ₃ OH) ₃]NO ₃	40 500	35 600	$ \begin{array}{r} \nu_3 & 24 \ 272* \\ \nu_2 & 14 \ 800, \ 12 \ 850 \ (Sh) \\ \nu_1 & 8 \ 200 \end{array} $				
[Ni(HPPD) ₂]	40 850	35 500	$v_3 24 300 + v_2 15 000, 1300$ (Sh) $v_1 9 400$				
[Co(HPPD)(CH ₃ OH) ₃]NO ₃	40 2 50	35 2 50	$\begin{array}{c} v_3 & 22\ 600 \\ v_2 & 18\ 400 \\ v_1 & 8\ 540 \end{array}$				
[Co(HPPD) ₂]	40 500	35 300	$\begin{array}{ccccccc} v_3 & 20 & 400 \\ v_2 & 19 & 250 \\ v_1 & 9 & 000 \end{array}$				
[Mn(HPPD)(CH ₃ OH) ₃]CH ₃ COO	39 850	35 750	$\frac{17\ 250}{22\ 000}$				
$[Mn(HPPD)_2]$	40 000	34 900	18 200 23 500				
[Cu(HPPD)CH ₃ OH]	39 2 50	34 600	19 250 15 600 12 500				
[Cu(HPPD) ₂]	39 800	35 000	21 000 14 625 11 200				
$[Fe(HPPD)(H_2O)_3]ClO_4$	40 300	35 250	23 800* 16 700* 9 800				
$[Fe(HPPD)_2]$	40 500	35 400	23 250* 16 000*				

Table II							
Assignment	of the	electronic	spectral	bands	of	HPPD	chelate:

* Charge-transfer bands

+ Calculated

for cobalt(II) chelates. The ratio of v_2/v_1 equals to 2.15 in conformity with accepted value for octahedral geometry [19].

11 250

In Mn(II) chelates the absorption bands at 17 250–18 200 cm⁻¹ and 22 000–23 500 cm⁻¹ have been assigned to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g(G)}$ and ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g(G)}$ transitions, respectively [20]. The other d-d transitions on higher energy side can not be observed as strong band of the ligand mask them.

As already stated, the Fe(II) chelates under consideration show two intense bands on the low energy side $(16\ 000-23\ 800\ \text{cm}^{-1})$ due to charge transfer and only one weak band at $9800-11\ 250\ \text{cm}^{-1}$ is observed which could be due to d-d transition, and can be ascribed to transition ${}^{5}T_{2g} \rightarrow {}^{5}T_{2g}$ [21]. Thus indicating that Fe(II) chelates have high spin octahedral geometry.

It is not possible to assign coordination geometry to 4-coordinate Cu(II) complexes on the basis of magnetic moment. However, the electronic spectra may distinguish between tetrahedral and square planar geometry. The tetrahedral Cu(II) complexes [22] exhibit only one absorption band in the near infrared region whereas square planar complexes show three bands on the low energy side of the electronic spectra. The chelates under investigation exhibit three weak bands (Table II) in the regions 19 250-21 000, 14 625-15 620 and 11 200-12 500 cm⁻¹ which may be assigned to transition [23-24] from ${}^{2}B_{1g}$ state to ${}^{2}B_{2g}$, ${}^{2}E_{g}$ and ${}^{2}A_{1g}$. respectively. Thus we may conclude that these copper chelates have square planar geometry.

The electronic spectral data were used to calculate 10 Dq, Racah parameter B, C, nephelauxetic ratio β, β° (%) and ligand field stabilisation energy (L. F. S. E.) [17, 20, 25] (see Table III).

A comparison of 10 Dq values for 1 : 2 Ni(II), Co(II), Fe(II) and Mn(II) chelates with representative values for various ligands indicates that the HPPD ligand has a place near water in spectro-chemical series [26] for the ligands. Further, the 10 Dq values for various metal ions follows the order: Fe(II) > Ni(II) > Co(II) > Mn(II) which is in accordance with the spectro-chemical series [26].

Chelates	10 vq cm ⁻¹	B ¹ cm ⁻¹	C^1 cm ⁻¹	<u>β</u>	٤° (%)	L.F.S.E. (KJ mol ⁻¹)
[Ni(HPPD)(CH ₃ OH) ₃]NO ₃	9200	766	3447	0.71	29.0	130.9
[Ni(HPPD) ₂]	9 400	768	3456	0.71	29.0	133.1
[Co(HPPD)(CH ₃ OH) ₃]NO ₃	9 396	1044	4071	0.93	7.0	67.5
[Co(HPPD)2]	8 487	943	3677	0.84	16.0	61.0
[Mn(HPPD)(CH ₃ OH) ₃][CH ₃ COO]	7 900	719	2516	0.75	25.0	_
[Mn(HPPD) ₂]	8 340	758	2653	0.79	21.0	
$[Fe(HPPD)(H_2O)_3]ClO_4$	9 800	490	2009	0.46	54.0	47.0
[Fe(HPPD) ₂]	11 250	562	2304	0.53	46.98	53.8
	1		1		1	1

Table III

Various electronic spectral parameters of 1:1 and 1:2 HPPD chelates

I. R. Spectra

The important absorption bands observed in the I. R. spectra of the chelates and the ligand are given in Table IV. The spectra of all chelates except of copper show similar features indicating that they are isostructural. From the structure of the ligand it appears that it can function as tridentate ligand with one phenolic oxygen, one nitrogen of the hydrazono group (-NH-N=C- and oxygen of the >C=0 group as possible interaction sites. The I. R.

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Chelates	v OH cm ⁻¹	$\nu \mathrm{NH} \atop \mathrm{cm}^{-1}$	$\nu N = C$ cm ⁻¹	v C=0 cm ⁻¹	ν C—0 cm ⁻¹	Methanolic
HPPD	3400	3200	1610	1680	1240	_
$[Fe(HPPD)(H_2O)]]ClO_4$		3200	1600	1650	1255	3460
[Mn(HPPD)[CH ₃ OH)] ₃ CH ₃ COO		3200	1590	1645	1245	3440
[Ni(HPPD)(CH ₃ OH) ₃]NO ₃		3200	1605	1650	1260	3440
[Co(HPPD)(CH ₃ OH) ₃]NO ₃		3200	1595	1640	1250	3450
[Cu(HPPD)(CH ₃ OH)]		-	1610	1660	1270	3460
[Fe(HPPD) ₂]		3200	1590	1645	1260	_
[Mn(HPPD) ₂]		3200	1600	1650	1250	-
[Ni(HPPD) ₂]		3200	1585	1655	1265	
[Co(HPPD) ₂]		3200	1595	1660	1255	
[Cu(HPPD) ₂]	3400		1610	1650	1240	

Some important infrared spectral bands of HPPD and its 1:1 and 1:2 chelates

spectrum of the ligand shows a strong band at 3200 cm⁻¹ which may be assigned to vNH [27]. In order to avoid mixing up of vNH assignment with vOH assignment, the vNH assignment was done on the basis of the I. R. spectra of similar compounds having no -OH group. The vNH stretching band remains intact in the spectra of all the chelates suggesting that -NH group is not involved in coordination.

A broad -OH stretching band [28] was observed at slightly lower frequency (3400 cm^{-1}) evidently due to hydrogen bonding [29, 30]. This band disappeared in the chelates indicating that proton is liberated on complex formation and phenolic oxygen is coordinated to the metal atom [31]. The coordination of phenolic oxygen to the metal is further confirmed by the shift of the phenolic C-O band (vC-O ligand 1240 cm⁻¹) to higher frequencies 1245 - 1265 cm⁻¹ in all the chelates [32]. Increase in ν C-O values was found to follow the order $Cu^{2+} > Ni^{2+} > Fe^{2+} > Co^{2+} > Mn^{2+}$. Similar order of stability has been observed by pH-metric method indicating that similar chelates are formed in the solid as well as in liquid phase [33]. Further the strong band at 1010 cm⁻¹ assigned to C=N stretching mode of azomethine linkage [34] was found to be shifted $(15-30 \text{ cm}^{-1})$ to lower frequency in all the chelates indicating the participation of azomethine nitrogen in coordination [35]. The $\nu C = 0$ stretching frequency at 1680 cm⁻¹ in the spectra of the ligand was lowered by $(20-40 \text{ cm}^{-1})$ in the spectra of all the chelates suggesting that $\nu C = 0$ group is involved in chelation. The appearance of a new band at 3440 - 3460 cm⁻¹ in case of 1 : 1 chelate is attributed to vOH of coordinated methanol/H₂O molecules [33].

The I. R. spectra of Cu(II) - 1:1 and 1:2 chelates are significantly different. In the spectra of 1:1 Cu-chelate, the NH and phenolic OH stretching bands were found to be absent suggesting that both these proton are released, on chelation. The $\nu C=O$ band at 1680 cm⁻¹ in the ligand shifted to lower frequency (1650 cm⁻¹) showing that the oxygen of the carbonyl group is coordinated to copper whereas the band due to -N=C stretch remains intact. Thus HPPD acts as a tridentate ligand with different bonding sites in the 1:1 copper chelate. The following structures are suggested.



(Typical structure of other chelates)

This type of interesting behaviour that the proton of the hydrazono group is released on chelation has also been observed by EVANS *et al.* [7], with 1:1 copper chelate of 3-phenylhydrazono-acetylacetone and its *ortho* carboxy derivative.

The I. R. spectra of 1:2 Cu-chelate shows that the vOH stretching band at 3400 cm⁻¹ remains intact while the vNH stretching band disappears and vC=O band at 1680 cm⁻¹ is shifted to lower frequencies indicating tridentate behaviour of the ligand. The 1:2 copper chelate has structure (I) which is significantly different from other (II).



EVANS et al. [7] also observed that the hydrazono ligand (2-carboxyphenyl hydrazonoacetylacetone) which acted as a tridentate ligand in 1:1 Cu-chelated behaved as a bidentate one in 1:2 copper chelate with nitrogen of the hydrazone and oxygen of the >C=O group at coordinating sites.

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A NEW METHOD FOR THE PREPARATION OF (2,2-DIPHENYLVINYLIDENE)-TRI--PHENYLPHOSPHORANE AND ITS REACTION WITH CARBONYL COMPOUNDS

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Hexaphenylcarbodiphosphorane (I), prepared from triphenylphosphine and carbon tetrahalide, when treated with benzophenone in equimolar ratio, gave the ylide (2,2-diphenylvinylidene)triphenylphosphorane (II) which, upon further treatment with benzophenone, gave 1,3-tetraphenylallene (III) via Wittig reaction.

The ylide (2,2-diphenylvinylidene)triphenylphosphorane (II) was first reported by GILMAN and TOMASI [1]. They have prepared it from the salt (2,2-diphenylvinylidene) triphenylphosphonium bromide. Here we report its preparation from hexaphenylcarbodiphosphorane (I) and benzophenone taken in equimolar amounts.

$$I \xrightarrow{C_6H_5} (C_6H_5)_3 P = C = P(C_6H_5)_3 + O = C \xrightarrow{C_6H_5} (C_6H_5)_3 P = C \xrightarrow{P} (C_$$

The formation of II was further confirmed by the addition of another mole of benzophenone, whereupon it gave 1,3-tetraphenylallene (III).

 $II + (C_6H_5)_2C = O \longrightarrow (C_6H_5)_2C = C = C(C_6H_5)_2 + Ph_3PO$ III

Hexaphenylcarbodiphosphorane (I) was prepared from a four-fold excess of triphenylphosphine and carbon tetrachloride.

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 $2 (C_6H_5)_3 P + CCl_4 \longrightarrow (C_6H_5)_3 P = CCl_2 + (C_6H_5)_3 PCl_2$ IV

 $IV + 2(C_6H_5)_3P \longrightarrow (C_6H_5)_3P \Longrightarrow C \Longrightarrow P(C_6H_5)_3 + (C_6H_5)_3PCl_2$

I

The structures of I and III have been confirmed by melting points, IR spectra and elemental analyses, comparing them with the literature values.

Experimental

Preparation of hexaphenylcarbodiphosphorane (I)

Triphenylphosphine (0.04 mole) was dissolved in dried and distilled benzene (50 mL) and carbon tetrachloride (0.01 mole) was added to the solution. An intense orange colour developed indicating the formation of the dihalo ylide **IV**, but the solution soon became colour-less. After two days, the reaction mixture was filtered, the filtrate was concentrated and chromatographed on a silica gel column. The carbodiphosphorane (I) was recrystallized from benzene. Its melting point was found to be 210-212 °C (*lit.* [2] m.p. 208-210 °C). $C_{37}H_{30}P_{2}$. Calcd. C 82.8; H 5.6; P 11.5. Found C 83.01; H 5.9; P 12.0%.

Preparation of (2,2-diphenylvinylidene)triphenylphosphorane and its reaction with benzophenone

Hexaphenylcarbodiphosphorane (0.01 mole) and benzophenone (0.01 mole) were taken up in dried and distilled petroleum ether (100 mL) and the resulting mixture was stirred for 2 h at 40-50 °C. The reaction mixture had an intense dark red colour indicating the formation of **II**. Benzophenone (0.01 mole) was then added again, and the resultant mixture was stirred for another 2 h at slightly raised temperature. The reaction mixture was then filtered, the filtrate concentrated and then subjected to column chromatography using silica gel as adsorbent. Tetraphenylallene was obtained in 38% yield (with respect to triphenylphosphine) and was recrystallized from acetone. Its m.p. was found to be 164-165 °C (*lit.* [1] m.p. 164-165 °C).

C27H20. Calcd. C 94.18; H 5.8; Found C 94.5; H 5.5%.

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ION-SOLVENT INTERACTIONS IN AQUEOUS SOLUTIONS OF ISOMERIC NITRO-BENZOATE IONS AND NITROBENZOIC ACIDS

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Relative viscosities of aqueous solutions of sodium salts of o-, m- and p-nitrobenzoic acids have been measured in the temperature range 25-35 °C to understand the effect of position isomerism on ion-solvent interaction. Of the free acids, the viscosity behaviour of o- and m-isomers only has been studied. As in acetic acid-acetate ion and benzoic acid-benzoate ion systems here also for a particular isomer the Bcoefficient of the acid is less than that of the anion of the same acid at a particular temperature. From the values of $B_{\rm salt}$ and $B_{\rm anion}$ the nitrobenzoate salts and nitrobenzoate anions can be arranged in the following order of increasing ion-solvent interactions

p-nitrobenzoate < o-nitrobenzoate < m-nitrobenzoate

demonstrating clearly the effect of the position of substituents on solute-solvent interactions. The energy of activation data supports this conclusion. The larger ion-solvent interaction in the case of the *meta*-isomer is ascribed to its greater size, being confirmed by the value of its partial molal volume, which is larger than those of the o- and p-isomers.

Introduction

The studies on the viscosity B-coefficients of aqueous solutions of acetic acid and alkali metal acetates by various workers [1, 2] reveal that the Bcoefficient of acetate ion (0.25) is much larger than that of the acetic acid molecule (0.12). It has been tentatively assumed that this is due to an enhanced order-producing nature of the acetate ion and not to any effect of size since the acetic acid molecule is almost identical in size with the acetate ion. Similar behaviour has also been observed in aqueous solution for benzoic acid molecule and benzoate ion [3, 4]. We have been studying in our laboratory the effect of position isomerism on ion-solvent interactions from the viewpoint of changes in the JONES-DOLE viscosity B-coefficient of substituted benzoic acids and their salts. We report in the present communication the results of viscometric studies on aqueous solutions of o- and m-nitrobenzoic acids at 25 °C and sodium salts of the corresponding acids including that of the paraisomer in the temperature range of 25-35 °C.

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Experimental

Pure isomeric nitrobenzoic acids obtained by repeated crystallization of corresponding nitrobenzoic acids (A. R. Grade) from triple distilled water were used for the preparation of the Na-salts of nitrobenzoic acids. Equivalent amounts of pure nitrobenzoic acid and sodium carbonate (Analar grade) were mixed in a minimum volume of water to obtain a clear solution from which the salt was slowly crystallized. The repeatedly crystallized product was finally washed several times with distilled ether and dried. Stock solutions of the Na-salts of isomeric nitrobenzoic acids were prepared from the dried salts by direct weighing. Solutions of varying concentrations were then prepared from the stock solutions by dilution. Densities of solutions were measured by a calibrated weld-type pyknometer (40 mL) provided with a graduated stem fitted with a standard joint stopper at its upper end. All viscosity measurements were made in a specially designed long flow time viscometer that was placed in a thermostat regulated within +0.005 °C. Efflux times of solutions were measured by a 1/10th second stopwatch and were reproducible to within ± 0.2 s. For the calibration of the viscometer the measured flow times of fresh triply distilled water at two different temperatures, viz., 30 and 35 °C are 867.8 and 785.5 s, respectively. The viscometer constants were determined according to the equation

$$\eta/d = A't - B'/t \tag{1}$$

where η (cP) is the viscosity, d is the density (g cm⁻³) and t is the flow time in seconds. The viscometer constants A' and B' are 9.299.10⁻⁴ and 5.21109, respectively.

Results and Discussion

The experimental data on relative viscosities of aqueous solutions of sodium salts of isomeric nitrobenzoic acids have been analyzed according to the JONES-DOLE [5] equation (2):

$$\eta/\eta_0 = 1 + AC^{1/2} + BC \tag{2}$$

where η/η_0 is the relative viscosity of a solution of concentration C mol/L, A and B are constants characteristic of the electrolyte and represent the ionion and ion-solvent interactions, respectively. The values of A and B coefficients evaluated from the intercept and slope respectively of the plot of $(\eta/\eta_0 - 1)/C^{1/2}$ versus $C^{1/2}$ are recorded in Table I, while the plots are shown in Figures 1, 2 and 3, respectively.

Empirical equation (3) is fitted to the densities (d) of the solutions by a least squares procedure

$$d = d_0 + \alpha m + \beta m^2 \tag{3}$$

where d_0 is the density of pure water, m is the solute molality and α , β are constants. The latter are shown in Table II which records also the values of the apparent molal volumes of solutes at infinite dilution (Φ_v^0) obtained graphically (not shown).

The *B*-coefficients of nitrobenzoate ions, calculated by KAMINSKY's procedure [6] and listed in column 3 of Table I, clearly demonstrate that the *B*-value of a particular nitrobenzoate ion is greater than that of the respective









Fig. 3. Plot of $\eta_{sp}/\sqrt{c} vs. \sqrt{c}$

nitrobenzoic acid, although the sizes of the anion and the acid are almost equal. Owing to the low solubility of *p*-nitrobenzoic acid in water in the temperature range studied the measurement could not be made. Similar observations were made earlier by LAWRENCE and WOLFENDEN [2] in the case of the acetic acid-acetate ion system, and by MANDAL *et al.* [3] for the benzoic acid-benzoate ion system.

The B-coefficients of both the salts and anions decrease with increasing temperature, suggesting a net structure making behaviour of the salts and the anions concerned. It is evident from Table I that the B-values of all the nitrobenzoate ions, instead of having a unique value at a particular temperature assume different values for different relative positions of the substituents. The observed B-values of nitrobenzoate salts and nitrobenzoate ions follow the order m - > o - > p-at each temperature. The larger ion-solvent interaction observed in the case of the meta-isomer may partly be ascribed to its greater size, which is confirmed by the value of its apparent molal volume at infinite dilution (Φ_v°) being larger than the corresponding values of the sodium salts of o- and p-nitrobenzoic acids. This is also supported by the effective volumes of the nitrobenzoate salts calculated from viscosity data using VAND's equation [7]. VAND's volumes are much greater than the values of Φ_v° . The larger intrinsic volume of the meta-nitrobenzoate salt is believed to be due to its greater preference for hydration relative to the ortho- and para-isomers.

	1 1		
1 3	h	e	

A		В		Banion			ΔE_{salt} ΔE_{salt}	$\Delta E_{\rm anion}^{\pm}$		
25 °C	30 °C	35 °C	25 °C	30 °C	35 °C	25 °C	30 °C	35 °C	25 °C	25 °C
0.0015	0.001	0.004	0.500	0.489	0.451	0.414	0.403	0.366	1100	1020
0.0065	0.0045	0.01	0.625	0.604	0.581	0.539	0.518	0.496	1970	1880
0.0075	0.012	0.001	0.469	0.457	0.431	0.383	0.371	0.346	996	912
0.002	_	_	0.389	-	-					
0.003	_	-	0.343	_	-					
	25 °C 0.0015 0.0065 0.0075 0.002 0.003	A 25 °C 30 °C 0.0015 0.001 0.0065 0.0045 0.0075 0.012 0.002 - 0.003 -	A 25 °C 30 °C 35 °C 0.0015 0.001 0.004 0.0065 0.0045 0.01 0.0075 0.012 0.001 0.002 - - 0.003 - -	A 25 °C 30 °C 35 °C 25 °C 0.0015 0.001 0.004 0.500 0.0065 0.0045 0.01 0.625 0.0075 0.012 0.001 0.469 0.002 - - 0.389 0.003 - - 0.343	A B 25 °C 30 °C 35 °C 25 °C 30 °C 0.0015 0.001 0.004 0.500 0.489 0.0065 0.0045 0.01 0.625 0.604 0.0075 0.012 0.001 0.469 0.457 0.002 - - 0.389 - 0.003 - - 0.343 -	$\begin{tabular}{ c c c c c c c } \hline A & & & & & & & & & & & & & & & & & &$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$

Values of viscosity coefficients A and B of (i) Na-salts of isomeric nitrobenzoic acids and (ii) o- and m-nitrobenzoic acids. Energy of activation for viscous flow of nitrobenzoate salts and nitrobenzoate ions

Table II

$v_{alues} of \alpha, p, \varphi_n$, hydration number and effective volume	Values	of	α . β . Φ°_{*}	. hydration	number	and	effective	volume
---	--------	----	---	-------------	--------	-----	-----------	--------

Solute		α		β		Øÿ			Hydration number	Effective molar volume	
	25 °C	30 °C	35 °C	25 °C	30 °C	35 °C	25 °C	30 °C	35 °C	25 °C	cm ³ mol ⁻¹ 25 °C
Na-o-nitrobenzoate	0.0856	0.0780	0.0712	-0.1078	0.0385	0.1328	101.2	112.5	121.5	3.4	219
Na-m-nitrobenzoate	0.1226	0.1114	0.1035	-0.2236	-0.0532	0.0644	117	130.7	141	5.3	317.6
Na-p-nitrobenzoate	0.0891	0.0825	0.2272	-0.0669	0.0838	0.0781	99	108.5	115	2.9	205
o-nitrobenzoic acid	0.0566	-	_	-0.3172	-	-					
m-nitrobenzoic acid	-0.0010	-	-	0.0671	_	-					
				1							

 $d_{00}^{25^\circ C}=0.99707;\, d^{30^\circ C}=0.99567 \text{ and } d_0^{35^\circ C}=0.99406$

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Calculation of the degree of hydration from viscosity data [8] has confirmed this. The fact that, of three isomeric nitrobenzoate salts, sodium *meta*-nitrobenzoate is hydrated even in the solid state [9] lends further support to this. Following NIGHTINGALE, Jr., and BENCK [10], we have calculated the energy of activation for viscous flow for the nitrobenzoate salts and nitrobenzoate ions.

The results shown in columns 5 and 6 of Table I support the conclusion made above. A look at the B values of ortho- and meta-nitrobenzoic acids immediately reveals that the former is a greater structure maker than the meta-isomer, a behaviour quite opposite to that noticed in case of their salts and anions.

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KINETICS OF REACTIONS OF \dot{C}_3 , \dot{C}_5 AND \dot{C}_7 ALKYL RADICALS FORMED IN THE $\dot{C}F_3 + C_2H_4$ SYSTEM, I

DETERMINATION OF THE RATE COEFFICIENTS

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n-Propyl, *n*-pentyl and *n*-heptyl free radicals (with perfluorinated methyl groups) were generated by the photolysis of perfluoroacetic anhydride (PFAA) in the presence of ethylene. Reaction products up to dodecanes were identified and measured under various experimental conditions, *i.e.* at different ethylene concentrations, $[C_2H_4]/[PFAA]$ ratios, reaction temperatures and incident light intensities. Disproportionation/ combination ratios were obtained for the *n*-propyl, *n*-pentyl and *s*-heptyl free radicals. The rates of addition of the C_3 and C_5 radicals were studied at 300 and 362 K. The rate coefficient ratios $k_{addition}/k_{L_c}^{1/2}$ mbination of $(4.04 \pm 0.69) \times 10^{-3}$ and $(2.72 \pm 0.66) \times 10^{-3}$ dm^{3/2} mol^{-1/2} s^{-1/2} were determined at room temperature for the *n*-propyl and *n*-pentyl radicals, respectively. The activation energies obtained were 27.8 kJ mol⁻¹ for C_3 addition and 26.8 kJ mol⁻¹ for C_5 addition. Isomerization rate coefficient relative to that of \dot{C}_7 self-combination, $k_{\rm isomeriz}/k_{\rm comb}^{1/2} = (5.8 \pm 1.0) \times 10^{-5}$ mol^{1/2} dm^{-3/2} s^{-1/2}, was determined at room temperature for addition and isomerization reactions are discussed in the light of available literature data.

Introduction

It has been suggested many times in the literature dealing with the pyrolysis of hydrocarbons that low molecular weight products may be formed via oligomerization processes consisting of consecutive addition, isomerization and decomposition reaction sequences. However, the experimental verification of such processes is very difficult since the formation of the reaction products may usually occur via different routes. Consequently, the interpretation of the reaction mechanism has to be based on the knowledge of the kinetic parameters of elementary reactions involved.

Kinetic data for hydrogen atom abstraction and decomposition reactions of alkyl radicals are rather well established, whereas there have been relatively few detailed kinetic studies of the isomerization and addition reactions of alkyl radicals. This is especially so for \dot{C}_5 and other free radicals of high carbon atom number. The difficulty of studying the kinetics of isomerization and addition reactions of long-chain alkyl radicals consists in the requirement that the radicals formed in these reactions have to be accounted for quantita-

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tively. The methods usually applied assume complete and accurate analysis of the numerous reaction products.

In the present work, kinetic data have been determined for addition, isomerization, disproportionation and combination reactions of alkyl radicals formed in the $\dot{C}F_3 + C_2H_4$ system. Radical additions to ethylene produce new free radicals with two more carbon atoms than the original ones. In this way consecutive additions yielded *n*-propyl, *n*-pentyl and *n*-heptyl (and *via* isomerization *s*-heptyl) free radicals in proportions which were dependent on the experimental conditions. Trifluoromethyl radicals were used instead of $\dot{C}H_3$ for the following reasons: (i). The photolysis of perfluoroacetic anhydride [1] proved to be a simple and clean source of $\dot{C}F_3$ which was free from any complications; (ii) Fluorine labelling facilitated the identification of the reaction products.

Experimental

Perfluoroacetic anhydride and ethylene (Fluka AG) were degassed and purified by bulb-to-bulb distillation in vacuum. Hexafluoroethane, trifluoromethane and 1,1,1-trifluoropropene (PCR Research Chem. Inc.) were used for identification and calibration purposes without further purification. Perfluoromethylcyclohexane (Pierce Chem. Co.) served as internal gas chromatographic standard.

Perfluoroacetic anhydride + ethylene + perfluoromethylcyclohexane mixtures were prepared in a conventional vacuum apparatus (equipped with PTFE valves) using different calibrated volumes. Experiments were carried out in a 83 cm³ cylindrical quartz cell equipped with planeparallel ULTRASIL windows. In order to keep the temperature constant during a run, the reaction cell was surrounded by an air thermostat. Temperature was regulated by means of a feed-back system controlled by a platinum resistance thermometer. Thus, temperature was kept constant within ± 0.5 K. A parallel light beam from a HANOVIA 500 W (Type 673 A) mercury are was used to produce the CF_3 radicals by the photolysis of the perfluoroacetic anhydride. Visible light was removed by a NiSO₄-CoSO₄ filter [2]. Light intensities were checked by a vacuum photocell.

After irradiation, reaction products were led through a trap which was cooled to liquid nitrogen temperature. Condensable products were transferred to a heated gas chromatographic sampling valve. Condensation was avoided by heating the trap, connecting tube and valve to 370 K.

Quantitative analysis of the numerous reaction products required the use of 15 m and 30 m Squalane SCOT columns at three temperatures (273, 353 and 373 K). Flame ionization detection was used and product peak areas were measured against the peak area of the internal standard.

Product identifications were based on the mass spectra taken on a FINNIGAN 1015 SL GC/MS instrument. Retention times of authentic samples as well as the Kovars' indices were used to check the identifications. (The Kovars' indices of the tri- and hexafluorinated products were found to be similar to those of the corresponding hydrocarbons.) Calibration factors used in the quantitative analyses were either determined experimentally with samples of known composition or estimated using the idea of "effective carbon number" [3].

Results and Discussion

Routes of product formation

In order to establish the free radical reactions occurring in the system, the product distribution and rates of formation have been determined in reaction series where (i) the concentration ratio of C_2H_4 and perfluoroacetic

Table I

	Product	[C ₂ H ₄]/[PFAA]	[C ₂ H ₄]/[PFAA]	[C2H4]/[PFAA]	[C2H4]/[PFAA]	
Design.	Formula	0.05	1	10	50	
C ₃ P	CF ₃ CH ₂ CH ₃	8.2	9.5	6.5	smalll	
C ₃ O	CF ₃ CH=CH ₂	8.0	9.8	5.3	smal	
C ₅ P	CF ₃ (CH ₂) ₃ CH ₃	0.2	0.5	3.6	5.9	
C ₅ O	$CF_3(CH_2)_2CH = CH_2$	0.2	0.5	3.4	5.3	
C ₇ P	CF ₃ (CH ₂) ₅ CH ₃	small	0.3	0.7	2.6	
C70	CF ₃ (CH ₂) ₄ CH=CH ₃	small	0.1	0.4	2.2	
	CF ₃ CH=CH(CH ₂) ₃ CH ₃					
C ₇ ON	CF ₃ CH ₂ CH=CH(CH ₂) ₂ CH ₃	small	small	0.4	1.4	
C ₆	$CF_3(CH_2)_4CF_3$	83.0	71.0	49.7	30.8	
C ₈	CF ₃ (CH ₂) ₆ CF ₃	0.4	7.8	21.9	29.4	
C10	CF ₃ (CH ₂) ₈ CF ₃	small	0.4	5.0	11.2	
C12	$CF_{3}(CH_{2})_{10}CF_{3}$	small	small	0.4	2.0	
	CH ₂ CH ₂ CF ₃					
iC10	CF ₃ CH ₂ CH(CH ₂) ₃ CH ₃	small	0.1	1.9	4.7	
	CH ₂ (CH ₂) ₃ CH ₃	X				
iC ₁₀	CF ₃ CH ₂ CH(CH ₂) ₃ CH ₃	small	small	0.8	4.5	

Reaction product distribution (%) obtained at various $[C_2H_4]/[PFAA]$ ratios. Temperature: 300 \pm 1 K, overall pressure: 6.7 \pm 0.1 kPa

anhydride (PFAA) was varied from 0.01 to 50 at 300 and 363 K temperatures; (ii) the temperature was varied from 300 to 440 K at $[C_2H_4]/[PFAA]$ ratios of 1 and 10, respectively; (iii) the light intensity was increased by more than an order of magnitude; and (iv) overall pressure was increased by increasing the reactant concentration or adding CO_2 or perfluoromethylcyclohexane as inert gases.

Product distributions obtained with different initial $[C_2H_4]/[PFAA]$ concentration ratios are shown in Table I. The results presented in the Table, which are averages of three or more experiments, are typical for the products and their relative rates of formation that are observed in the $\dot{C}F_3 + C_2H_4$ system. Altogether 13 hydrocarbon reaction products were detected and measured in this work. Their formulas and the designations we shall use further on are given in columns 2 and 1, respectively. It may be seen that the product spectrum ranges from the paraffins and olefins with three carbon atoms up to the *normal* and *iso*-dodecanes. CF_3H and C_2F_6 could not be detected either in the experiments presented in Table I or in other reaction series, indicating that the addition of $\dot{C}F_3$ radicals to the double bond of C_2H_4 is considerably faster under all experimental conditions investigated than any other reactions

of the trifluoromethyl radicals. On the other end of the product spectrum, the dodecanes were the highest molecular weight compounds which could be detected and measured. (Some underestimation of their amounts may not be excluded because of the unfavourable peak forms and minor losses on the capillary column used in the analysis. This may not have a significant effect on our results.) In experiments carried out at the highest $[C_2H_4]/[PFAA]$ ratios, there were some indications of the formation of even higher molecular weight products. However, their role is certainly insignificant.

The formation of the reaction products can be explained by reactions of four trifluoroalkyl radicals. Three of these are primary alkyl free radicals,

$CF_3CH_2\dot{C}H_2$	designated by $\dot{\mathrm{C}}_3$
$\mathrm{CF}_3(\mathrm{CH}_2)_3\dot{\mathrm{CH}}_2$	designated by $\dot{\mathrm{C}}_5$
$CF_3(CH_2)_5\dot{C}H_2$	designated by Ċ ₇ ,

which may be formed by successive additions to ethylene, and the forth is a secondary radical,

CF₃CH₂ĊH(CH₂)₃CH₃ designated by sĊ₇,

which may be derived from \dot{C}_7 by 1,5-hydrogen shift. The paraffin products with even carbon atom numbers and with two CF_3 groups (which appear in the last six rows of the Table) are definitely combination products, while the paraffin and olefin products with odd carbon atom numbers and with one CF_3 group in each molecule (see rows 1-7) originate from disproportionation reactions of the free radicals.

Formation of the products detected in this work can be explained by the following reaction scheme. (The designations used for the rate coefficients refer to the type of reaction in question, *i.e.* ad = addition, c = combination, d = disproportionation and i = isomerization. They also indicate the carbon atom number of the free radicals which react; in case of disproportionation reactions, the C-atom number of the H-abstracting radical is given first and that of the H-donating radical last.)

$$PFAA + h\nu \longrightarrow 2\dot{C}_1 + CO + CO_2 \tag{1}$$

$$\dot{C}_1 + C_2 H_4 \xrightarrow{k_{1ad}} \dot{C}_3 \tag{2}$$

$$\dot{C}_3 + \dot{C}_3 \xrightarrow{k_{BOB}} C_6$$
 (3)

 $\xrightarrow{K_{ads}} C_3 P + C_3 O \tag{4}$

$$\dot{\mathrm{C}}_3 + \mathrm{C}_2\mathrm{H}_4 \xrightarrow{k_{\mathrm{sad}}} \dot{\mathrm{C}}_5$$
 (5)

Ċ,

Ċ

$$\dot{\mathbf{C}}_5 + \dot{\mathbf{C}}_3 \xrightarrow{k_{\delta_63}} \mathbf{C}_8 \tag{6}$$

$$\xrightarrow{k_{3ds}} C_3 P + C_5 O \tag{7}$$

$$\xrightarrow{k_{sd3}} C_3 O + C_5 P \tag{8}$$

$$+ \dot{C}_5 \xrightarrow{k_{ses}} C_{10}$$
 (9)

$$\xrightarrow{k_{sds}} C_5 P + C_5 O \tag{10}$$

$$\dot{\mathbf{C}}_5 + \mathbf{C}_2 \mathbf{H}_4 \xrightarrow{k_{\text{sad}}} \dot{\mathbf{C}}_7 \tag{11}$$

$$C_7 + \dot{C}_3 \xrightarrow{k_{7cs}} C_{10}$$
 (12)

$$\xrightarrow{k_{\rm ad7}} C_3 P + C_7 O \tag{13}$$

$$\xrightarrow{k_{rds}} C_3 O + C_7 P \tag{14}$$

$$\dot{C}_7 + \dot{C}_5 \xrightarrow{k_{705}} C_{12}$$
 (15)

$$\xrightarrow{\kappa_{\mathbf{sd7}}} \mathbf{C_5P} + \mathbf{C_7O} \tag{16}$$

$$\xrightarrow{R_{7ds}} C_7 P + C_5 O \tag{17}$$

$$\dot{C}_7 \qquad \xrightarrow{k_{1i}} s\dot{C}_7 \qquad (18)$$

$$\dot{\mathrm{C}}_{7} + \dot{\mathrm{C}}_{3} \xrightarrow{k_{\mathrm{sres}}} i\dot{\mathrm{C}}_{10}$$
 (19)

$$\xrightarrow{R_{\text{sdsr}}} C_7 ON + C_3 P \tag{20}$$

$$\xrightarrow{\kappa_{erds}} C_7 P + C_3 O \tag{21}$$

$$s\dot{C}_7 + \dot{C}_5 \xrightarrow{R_{a7\,c5}} iC_{12}$$
 (22)

$$\xrightarrow{k_{\text{sd s7}}} C_7 ON + C_5 P \tag{23}$$

$$\xrightarrow{R_{\text{rrds}}} C_2 P + C_5 O \tag{24}$$

In this scheme, we have included the addition, isomerization, combination and disproportionation reactions of the four trifluoroalkyl radicals, with the exception of certain reactions of \dot{C}_7 and $s\dot{C}_7$. Among the latter ones only the major reactions are taken into account, *i.e.* reactions of \dot{C}_7 and $s\dot{C}_7$ with the abundant radicals \dot{C}_3 and \dot{C}_5 as well as $\dot{C}_7 \rightarrow s\dot{C}_7$ isomerization. Hydrogen atom abstraction reactions were not considered since they are of negligible importance at room temperature as evidenced by the similar rate of formation of paraffins and olefins with identical carbon atom number (see Table II). Around and above 400 K, especially in experiments carried out at high C_2H_4 concentrations the rates of formation of the paraffins were found to exceed

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Table II

Ratios of paraffins and olefins with identical carbon atom numbers as a function of the reaction temperature. $[C_2H_4]/[PFAA] = 1:1$, overall pressure: 6.7 \pm 0.1 kPa

301 K	364 K	438 K
	1	
0.96	1.23	1.42
1.16	1.59	1.77
	1.39	1.34
	301 K 0.96 1.16	301 K 364 K 0.96 1.23 1.16 1.59 1.39

those of the corresponding olefins and at the same time new peaks appeared on the chromatograms. All this indicates that hydrogen abstractions occurred and the mechanism became complicated at high temperatures. No indications of radical decomposition reactions were observed, at least below 400 K, therefore, decomposition reactions were not considered in the scheme.

As expected, combination products predominate under all experimental conditions. At 300 K they contribute $82 \pm 2\%$ to product formation, while only $18 \pm 2\%$ is accounted for by the disproportionation products. This means that $90 \pm 1.5\%$ and $10 \pm 1.5\%$ of the free radicals disappear by combination



Fig. 1. Dependence of combination product yields (percentage of total amount of products) on the $[C_2H_4]/[PFAA]$ ratio. Temperature: 300 ± 1 K; overall pressure: 6.7 ± 0.1 kPa. (1), C_6 ; (2), C_8 ; (3), C_{10} ; (4), C_{12} ; (5) iC_{10} ; (6), iC_{12}

and disproportionation reactions, respectively. While the ratio of all combination products to all disproportionation products is found to be practically constant at room temperature, the distribution of the combination as well as that of the disproportionation products depends considerably on the experimental conditions.

According to the reaction scheme, there is a competition between reactions second and first order with respect to radical concentration. (The former group consists of combination and disproportionation reactions, while additions and isomerization belong to the latter one.) Any change in the experimental conditions which influences the competition between reactions first and second order with respect to radical concentration is expected to alter the spectrum of free radicals and, as a consequence, the distribution of reaction products. Thus, for instance, an increase in the $[C_2H_4]/[PFAA]$ ratio or in temperature should favour additions as compared to combinations and disproportionations with the result of increasing the role played by radicals of higher carbon atom number and at the same time increasing also the percentage of higher molecular weight compounds in the product composition. An opposite effect is expected with increasing light intensity.

Figures 1 and 2 show the dependences of the yields of combination products and disproportionation products, respectively, on the initial composi-



Fig. 2. Dependence of disproportionation product yields (percentage of total amount of products) on the $[C_2H_4]/[PFAA]$ ratio. Temperature: 300 ± 1 K; overall pressure: 6.7 ± 0.1 kPa. (1), C_3P ; (2), C_3O ; (3), C_5P ; (4), C_5O ; (5), C_7P ; (6), C_7O ; (7), C_7ON

tion. It may be seen that an increase in the $[C_2H_4]/[PFAA]$ ratio enhances the formation of higher molecular weight products. This indicates the increase in the role played by radicals of higher carbon number with increasing ethylene concentration as a result of enhanced addition.

The dependence of the yields of combination products on the reaction temperature and on light intensity is presented in Figs 3 and 4, respectively. As can be seen, the distribution of the combination products shows the tendency expected on the basis of the suggested mechanism.



Fig. 3. Dependence of combination product yields (percentage of total amount of products) on reaction temperature. $[C_2H_4]/[PFAA] = 1:1$, overall pressure: 6.7 ± 0.1 kPa. (1), C_6 ; (2), C_8 ; (3), C_{10} ; (4), C_{12} ; (5), iC_{10} ; (6), iC_{12}

Free radical concentrations

Free radical concentrations can be derived from the experimental rates of formation of the combination products. Thus, for trifluoropropyl radical concentration one obtains

$$[\dot{\mathbf{C}}_3] = \frac{R^{1/2}(C_6)}{k_{3c3}^{1/2}} \tag{25}$$

Furthermore, relative concentrations of the higher free radicals are

$$\frac{[\dot{C}_5]}{[\dot{C}_3]} = \frac{k_{3c3}}{k_{5c3}} \frac{R(C_8)}{R(C_6)}$$
(26)

$$\frac{[\dot{C}_7]}{[\dot{C}_2]} = \frac{k_{5c3}}{k_{7c5}} \frac{R(C_{12})}{R(C_8)}$$
(27)

$$\frac{[s\dot{C}_{7}]}{[\dot{C}_{3}]} = \frac{k_{3c3}}{k_{s7c3}} \frac{R(iC_{10})}{R(C_{6})} = \frac{k_{5c3}}{k_{s7c5}} \frac{R(iC_{12})}{R(C_{8})}$$
(28)



Fig. 4. Dependence of combination product yields (percentage of total amount of products) on incident light intensity. $[C_2H_4]/[PFAA] = 1:1$, overall pressure: 6.7 \pm 0.1 kPa. (1), C₆; (2), C₈; (3), C₁₀; (4), C₁₂; (5), iC₁₀; (6), iC₁₂

Combination and disproportionation reactions

 C_3P and C_3O products are formed at room temperature only by disproportionation reactions of the \dot{C}_3 radicals. From the reaction scheme, by means of Eqs (25)-(28), one obtains

$$\frac{R(C_3P)}{R(C_6)} = \frac{k_{3d3}}{k_{3c3}} + \frac{k_{3d5}}{k_{5c3}} \frac{R(C_8)}{R(C_6)} + \frac{k_{3d7}}{k_{7c5}} \frac{k_{5c3}}{k_{3c3}} \frac{R(C_{12})}{R(C_8)} + \frac{k_{3ds7}}{k_{s7c3}} \frac{R(iC_{10})}{R(C_6)}$$
(29)

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and

$$\frac{R(C_3O)}{R(C_6)} = \frac{k_{3d3}}{k_{3c3}} + \frac{k_{5d3}}{k_{5c3}} \frac{R(C_8)}{R(C_6)} + \frac{k_{7d3}}{k_{7c5}} \frac{k_{5c3}}{k_{3c3}} \frac{R(C_{12})}{R(C_8)} + \frac{k_{s7d3}}{k_{s7c3}} \frac{R(iC_{10})}{R(C_6)}$$
(30)

In these expressions the last two terms can be neglected $[R(C_{12})/R(C_8) \ll 1]$ and $R(iC_{10})/R(C_6) \ll 1]$ and the equations take the simple linear forms

$$\frac{R(C_3P)}{R(C_6)} = \frac{k_{3d_3}}{k_{3c_3}} + \frac{k_{3d_5}}{k_{5c_3}} \frac{R(C_8)}{R(C_6)}$$
(29')

and

$$\frac{R(C_3O)}{R(C_6)} = \frac{k_{3d3}}{k_{3c3}} + \frac{k_{5d3}}{k_{5c3}} \frac{R(C_8)}{R(C_6)}$$
(30')

Plotting the experimental results measured at room temperature, the disproportionation/combination ratios

$$\frac{k_{3d3}}{k_{3c3}} = 0.10 \pm 0.01 \text{ and } \frac{k_{3d5}}{k_{5c3}} = \frac{k_{5d3}}{k_{5c3}} = 0.055 \pm 0.015$$
(31)

were obtained. (The error limits here and throughout the paper are at a 95% confidence level.)

The disproportionation/combination ratio for $\dot{C}_3 + \dot{C}_5$ can be derived also from a similar analysis of $R(C_5P)/R(C_8)$ and $R(C_5O)/R(C_8)$. The values obtained for k_{3d5}/k_{5c3} and k_{5d3}/k_{5c3} range between 0.05 and 0.08 in good agreement with the above results.

Product C_7ON is a measure of disproportionation reactions (20) and (23). The rate of formation of heptene with non-terminal double bond may be given as

$$R(C_{7}ON) = \frac{k_{3ds7}}{k_{s7c3}} R(iC_{10}) + \frac{k_{5ds7}}{k_{s7c3}} R(iC_{12})$$
(32)

With the reasonable assumption of $k_{3ds7} \simeq k_{5ds7}$, one obtains, from the $R(C_7ON)/$ / $R(iC_{10}) + R(iC_{12})$ ratios measured at room temperature,

$$\frac{k_{\rm 3ds7}}{k_{\rm s7c3}} = \frac{k_{\rm 5ds7}}{k_{\rm s7c5}} = 0.15 \pm 0.05 \tag{33}$$

A rough estimate of the disproportionation/combination ratios $\Delta(s\dot{C}_7, \dot{C}_3)$ and $\Delta(s\dot{C}_7, \dot{C}_5)$ can be obtained from

$$\frac{R(C_7P) - R(C_7O)}{R(iC_{10}) + R(iC_{12})} \simeq \frac{k_{s7d3}}{k_{s7c3}} = \frac{k_{s7d5}}{k_{s7c5}}$$
(34)

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Table III

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Source
[4], [5]
[6]
[6]
[7]

Disproportionation/combination ratios $[\Delta(\dot{R_1}, \dot{R_2}) = k_{\rm dis}/k_{\rm comb}, \text{ where } \dot{R_1} \text{ and } \dot{R_2} \text{ are } H \text{ donor and } H \text{ acceptor, respectively}]$

which involves the assumption of $k_{s7d3} = k_{s7d5}$. The considerable uncertainty of the value of ≥ 0.2 obtained for this disproportionation/combination ratio is due to the fact that the determination of the difference in rates of formation of two minor products (C₂P and C₂O) is required.

The disproportionation/combination ratios determined in this work are compared in Table III with literature data for related reactions. The \dot{C}_3 , \dot{C}_5 and $s\dot{C}_7$ radicals (with one fluorinated methyl group) show a behaviour similar to the corresponding alkyl free radicals regarding the disproportionation/ combination ratios.

Addition reactions

The rate coefficient for \dot{C}_3 addition to C_2H_4 [reaction (5)] can be calculated from the equation

$$R_{3ad} = R(\dot{C}_5) = k_{3ad}[\dot{C}_3][C_2H_4] = \frac{k_{3ad}}{k_{3c3}^{1/2}} R^{1/2}(C_6)[C_2H_4]$$
(35)

where $R(\dot{C}_5)$ designates the rate of formation of the \dot{C}_5 free radicals. According to the reaction scheme, the rate $R(\dot{C}_5)$ may be expressed in terms of measured rates of formation of stable reaction products as $R(\dot{C}_5) = R(C_8) + \frac{1}{4} \frac{R^2(C_8)}{R(C_6)} + R(C_{10}) + 2R(C_{12}) + R(iC_{10}) + 2R(iC_{12}) + R(C_5P) + R(C_5O) + R(C_7P) + R(C_7O) + R(C_7ON)$. In this expression of $R(\dot{C}_5)$, the term $\frac{1}{4} \frac{R^2(C_8)}{R(C_6)}$ accounts

for the rate of formation of C_{10} by self-combination of \dot{C}_5 radicals [reaction (9)], and use has been made of the geometric mean rule* $k_{5c3} = 2(k_{3c3}k_{5c5})^{1/2}$.

Using Eq. (35), we obtain $k_{3ad}/k_{3c3}^{1/2} = (4.04 \pm 0.069) \times 10^{-3}$ and $(2.73 \pm 0.79) \times 10^{-2} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ at 300 and 362 K, respectively. An estimation of the Arrhenius parameters based on kinetic data obtained at two temperatures yields

$$E_{3ad} - \frac{1}{2} E_{3c3} = 27.8 \text{ kJ mol}^{-1} \text{ and } A_{3ad} / A_{3c3}^{1/2} = 2.8 \times 10^2 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$
(36)

The rate coefficient for \dot{C}_5 addition to C_2H_4 [reaction (11)] was calculated from the equation

$$R_{\text{5ad}} = R(\dot{C}_7) = k_{\text{5ad}}[\dot{C}_5][C_2H_4] = \frac{1}{2} \frac{k_{\text{5ad}}}{k_{\text{5c5}}^{1/2}} \frac{R(C_8)}{R^{1/2}(C_6)} [C_2H_4]$$
(37)

in which we substituted $[\dot{C}_5]$ from Eq. (26) and made use of the geometric mean rule $k_{5^{C3}} = 2(k_{3^{C3}}k_{5^{C5}})^{1/2}$. In Eq. (37), $R(\dot{C}_7)$ designates the rate of formation of the \dot{C}_7 free radicals: $R(\dot{C}_7) = \left\{ R(C_{10}) - \frac{1}{4} \frac{R^2(C_8)}{R(C_6)} \right\} + R(C_{12}) + R(iC_{10}) + R(iC_{12}) + R(C_7O) + R(C_7ON)$, where the terms in braces $\{ \}$ account for the rate of formation of C_{10} by combination of \dot{C}_3 and \dot{C}_7 radicals.

From Eq. (37) we calculate $k_{\text{5ad}}/k_{\text{5c5}}^{1/2} = (2.72 \pm 0.66) \times 10^{-3}$ and $(1.67 \pm 0.79) \times 10^{-2} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ at 300 and 363 K, respectively. An estimation of the Arrhenius parameters based on these two rate coefficient ratios yields

$$E_{\rm 5ad} - \frac{1}{2} E_{\rm 5c5} = 26.8 \text{ kJ mol}^{-1} \text{ and } A_{\rm 5ad} / A_{\rm 5c5}^{1/2} = 1.3 \times 10^2 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$$
(38)

In Table IV, we compare our addition rate coefficients with literature date. SANGSTER and THYNNE reported [8] a high rate coefficient for the addition of 3,3,3-trifluoropropyl-1 radical to ethylene, which seems to indicate that the \dot{C}_3 radical behaves like the very reactive $\dot{C}F_3$ radical in addition reactions $(k_{\rm ad}/k_{\rm comb.}^{1/2} = 46 \, {\rm dm}^{3/2} \, {\rm mol}^{-1/2} \, {\rm s}^{-1/2}$ for $\dot{C}F_3$ at 300 K [9]). On the contrary, our rate coefficients $k_{\rm 3ad}$ and $k_{\rm 5ad}$ (which were derived from analytical data obtained under various experimental conditions, *i.e.* at different $[C_2H_4]/[PFAA]$ ratios, reactant concentrations and incident light intensities) as well

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^{*} With reasonable assumptions for the ratios of certain rate coefficients, it may be shown that the geometric mean rule holds for the combination of the \dot{C}_3 and \dot{C}_5 radicals. A detailed investigation of the correlation is not warranted in this system.

Table IV

Ŕ	$k_{\rm ad}/k_{ m comb}^{1/2}$ at 300 K	$E_{\rm ad} = \frac{1}{2} E_{\rm comb}$	$A_{\rm ad}/A_{\rm comb}^{1/2}$	Source
Ċ,	$4.0 \cdot 10^{-3}$	27.8	$2.8 \! imes \! 10^2$	this work
Ċ5	$2.8 imes 10^{-3}$	26.8	$1.3\! imes\!10^2$	this work
Ŕ	$k_{ m ad}/k_{ m comb}^{1/2}$ at 300 K	$E_{\mathrm{ad}} = rac{1}{2} E_{\mathrm{comb}}$	$A_{\rm ad}/A_{\rm comb}^{1/2}$	Source
Ċ ₃	12*			[8]
CH ₃ CH ₂ ĊH ₂	$9.0 imes 10^{-3}$	25.5	$2.5 imes10^2$	[9]
$CH_{3}CH_{2}CH_{2}\dot{C}H_{2}$	3.9×10 ⁻³	28.0	$3.0 imes10^2$	[9]

Rate coefficients for addition reactions. (Designation 'ad' and 'comb' refer to $\dot{R} + C_2H_4 \rightarrow RCH_2\dot{C}H_2$ and $\dot{R} + \dot{R} \rightarrow RR$ reactions; units used are mol, dm³, s and kJ.)

* Obtained from data given in Table I of ref.[9] with assumed value of $k_{\rm comb} = 10^{9.8}\,\rm dm^3$ mol^-1 s^-1

our Arrhenius parameters are similar to the kinetic data reported for alky¹ radical addition reactions.

The fact that we obtain kinetic data for the addition of \dot{C}_5 radical (having the F atoms so far removed from the site of the odd electron that it certainly behaves like an alkyl radical) which are close to those determined with the same technique for the addition of \dot{C}_3 to ethylene, strongly suggests that one expects the reactivity of the 3,3,3-trifluoropyl-1 radical to be similar to that of the *n*-propyl radical. Apart from this reasoning, one can easily show that if \dot{C}_3 added to ethylene as fast as suggested by SANGSTER and THYNNE, we could hardly find combination products of \dot{C}_3 and could not detect disproportionation products of \dot{C}_3 . The ratio of the rate of addition and self-combination is given by

$$\frac{R_{3ad}}{R_{3c3}} = \frac{k_{3ad}}{k_{3c3}^{1/2}} \frac{[C_2H_4]}{R^{1/2}(C_6)}$$
(39)

In a typical experiment at 300 K, $[C_2H_4]/[PFAA] = 10:1$ and $[C_2H_4] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$ we found the rate of formation of C_6 to be around $10^{-10} \text{ mol dm}^{-3} \text{ s}^{-1}$. Hence with $k_{3ad}/k_{3c3}^{1/2} = 12 \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1/2}$ (the value of SANGSTER and THYNNE) one obtains from Eq. (39) $R_{3ad}/R_{3c3} = 3 \times 10^3$, *i.e.* a negligible part of the products would be C_6 . On the contrary, we find C_6 to be the major reaction product.

It is hard to find an explanation for the three orders of magnitude differs ence in k_{3ad} . One reason may be the considerable overestimation of the amount of the minor product $CF_3CH_2CH_2CH_3$ in the analysis of SANGSTER and THYNNE due to the interference caused by an unresolved product or impurity.

Some indication of the overestimation is apparent from the unexpectedly high yield of $CF_3CH_2CH_2CH_2CH_3$ (17.6 times higher than that of $CF_3CH=CH_2$) found by SANGSTER and THYNNE in an experiment carried out in the absence of H_2S .

Isomerization

The rate coefficient for $\dot{C}_7 \rightarrow s\dot{C}_7$ isomerization [reaction (18)] can be calculated from the rates of product formation in reactions (20)-(24):

$$R_{7i} = R(s\dot{C}_{7}) = k_{7i}[\dot{C}_{7}] = \frac{k_{7i}}{k_{7c7}^{1/2}} \frac{R(C_{12}) R^{1/2}(C_{6})}{R(C_{8})}$$
(40)

In deriving Eq. (40), the expression for $[\dot{C}_7]$ has been taken from Eq. (27) and use has been made of the geometric mean rules $k_{5c3} = 2(k_{3c3}k_{5c5})^{1/2}$ and $k_{7c5} = 2(k_{5c5}k_{7c7})^{1/2}$, which allowed us to replace $k_{5c3}/(k_{7c5}k_{3c3}^{1/2})$ by $1/k_{7c7}^{1/2}$. The term $R(s\dot{C}_7)$ designates the rate of formation of the radical $s\dot{C}_7$ which may be given according to our reaction scheme by $R(s\dot{C}_7) = (1 + k_{s7d3}/k_{s7c3}) R(iC_{10}) +$ $+(1 + k_{s7d5}/k_{s7c5}) R(iC_{12}) + R(C_7ON)$. For the ratios k_{s7d3}/k_{s7c3} and k_{s7d5}/k_{s7c5} we estimated ≥ 0.2 (see above), furthermore, the values of 0.23 and 0.45 were reported for the disproportionation/combination ratios of analogous reactions (see Table III). Hence we may assume that $k_{s7d3}/k_{s7c3} = k_{s7d5}/k_{s7c5} = 0.35$. The use of this figure in the calculation of $R(s\dot{C}_7)$ may introduce an error of less than 10% in the isomerization rate coefficient.

Using the data measured at 300 K (in experiments carried out at $[C_2H_4]/[PFAA] \leq 10$ ratios, various reactant concentrations and light intensities), we obtain from Eq. (40)

$$\frac{k_{7i}}{k_{7c7}^{1/2}} = (5.8 \pm 1.0) \times 10^{-5} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1/2}$$
(41)

Measurements of the minor products (like C_{12} and C_7ON) were not accurate enough to derive reliable isomerization rate coefficients at higher temperatures, thus Arrhenius parameters could not be determined by experiment.

Inquiring into the sources of possible systematic errors, the neglect of addition of $s\dot{C}_7$ radicals to C_2H_4 has to be dealt with. Since we were unable to identify definitely products which could be formed in reactions of free radicals with nine carbon atoms, we omitted $s\dot{C}_7 + C_2H_4$ addition reaction from the reaction scheme and as a result we did not include a term for R_{s7ad} in the expression of $R(s\dot{C}_7)$ in Eq. (40). This might have caused an underestimation of $k_{7i}/k_{7c7}^{1/2}$. Although addition reaction $s\dot{C}_7 + C_2H_4$ could not be monitored directly by measuring the rates of formation of the appropriate high molecular

weight products, however, a reasonably good estimate of R_{s7ad} can be obtained* if $k_{s7ad}/k_{s7cs7}^{1/2}$ is assumed to be similar to $k_{5ad}/k_{5c5}^{1/2}$ or $k_{3ad}/k_{3c3}^{1/2}$. In this way it may be shown that the omission of $s\dot{C}_7 + C_2H_4$ addition causes an underestimation in $k_{7l}/k_{7c7}^{1/2}$ of about 0.5%, 3-6%, 10-21% and 50-100% in our experiments carried out at $[C_2H_4]/[PFAA]$ ratios of 0.05:1,1:1,10:1 and 50:1, respectively. Therefore, only data obtained at $[C_2H_4]/[PFAA] \leq 10$ were used to derive the isomerization rate coefficient $k_{7l}/k_{7c7}^{1/2}$. (It is to be mentioned that the neglect of addition reaction $\dot{C}_7 + C_2H_4$ may cause an underestimation in $k_{3ad}/k_{3c3}^{1/2}$ and $k_{5ad}/k_{5c5}^{1/2}$. However, it may be shown by considerations similar to the above ones that this is negligible under all experimental conditions.)

WATKINS and co-workers found that *n*-pentyl radicals [10] and *n*-hexyl radicals [11] formed by addition of smaller alkyl radicals to ethylene are chemically activated, thus vibrationally excited as well as thermalized free radicals may contribute to the observed rate of isomerization. We have not taken into account excited C₂ radical reactions in our reaction scheme, therefore, it is necessary to show that isomerization of chemically activated \dot{C}_7 radicals does not contribute to $\dot{\mathrm{sC}}_7$ formation under the experimental conditions used in this work. In a series of experiment we increased the overall pressure of the system (at constant $[C_2H_4]/[PFAA] = 50:1$ ratio by increasing the concentration of the reactants) from 6.7 to 32.7 kPa and calculated $k_{7i}/k_{7c7}^{1/2}$ from Eq. (40) as described above. The results are given in Table V. One expects $k_{7i}/k_{7c7}^{1/2}$ to decrease with pressure if chemically activated $\dot{
m C}_7$ radicals contribute to the observed rate of isomerization. As may be seen from the results presented in the Table, this is not the case under the experimental conditions of our investigations. As a matter of fact, the data seem to support an opposite tendency which we interpret simply as the result of experimental errors.

Our results on the 1,5-hydrogen shift (isomerization) of *n*-heptyl radicals may be compared with the data for the similar reaction of *n*-hexyl reported in the literature [12]. From experiments carried out in the presence of added SF₆ (high pressure) to ensure thermalization of the *n*-hexyl radicals, WATKINS [11] obtained log $(k_{6i}k_{2c2}^{1/2}k_{6c2}^{-1}/\text{mol}^{1/2} \text{dm}^{-3/2} \text{s}^{-1/2}) = 3.94 - 46.9 \text{ kJ/RT} \ln 10$, where k_{6i} , k_{2c2} and k_{6c2} designate the rate coefficients for thermal isomerization (1,5 hydrogen shift) of *n*-hexyl, for self-combination of ethyl and for cross combination of ethyl + *n*-hexyl, respectively. Assuming the geometric mean rule $k_{6c2} = 2(k_{2c2}k_{6c6})^{1/2}$ to be valid, the ratio $k_{2c2}^{1/2}k_{6c2}^{-1}$ may be replaced by $1/2k_{6c6}^{1/2}$ and the isomerization rate cofficient k_{6i} relative to the *n*-hexyl self-combination rate coefficient k_{6c6} can be expressed as log $(k_{6i} k_{6c6}^{-1/2}/\text{mol}^{1/2} \text{dm}^{-3/2} \text{s}^{-1/2}) =$ $= 4.24 - 46.9 \text{ kJ/RT} \ln 10$. This yields at 300 K $k_{6i}/k_{6c6}^{1/2} = 1.2 \times 10^{-4} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1/2}$ for *n*-hexyl radical in accordance with out result $k_{7i}/k_{7c7}^{1/2} = 5.8 \times$ $\times 10^{-5} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1/2}$ for *n*-heptyl radical.

* The rate of addition of $s\dot{C}_7$ to C_2H_4 may be given as $R_{s7ad} = \frac{1}{2} \frac{k_{s7ad}}{k_{s7cs7}^{1/2}} \frac{R(iC_{10})}{R^{1/2}(C_6)} [C_2H_4].$

One expects the pre-exponential factors for isomerization of *n*-heptyl and n-hexyl radicals to be very similar. With the reasonable assumption of $A_{7i}/A_{7c7}^{1/2} = A_{6i}/A_{6c6}^{1/2}$ and log $(A_{6i}/A_{6c6}^{1/2}) = 4.24$ taken from the work of WATKINS [11] the activation energy difference of $E_{7i} - 1/2 E_{7c7} = 48.7 \text{ kJ} \text{ mol}^{-1}$ is obtained from Eq. (41). However, $A_{6i}/A_{6c6}^{1/2} = 10^{4 \cdot 24} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1/2}$ is more

Table V

Isomerization rate coefficients obtained at various pressures. Reaction temperature: 300 K; $[C_2H_4]/[PFAA] = 50:1$

	$\Sigma p/\mathrm{kPa}$	6.7	27.0	32.7
${k_{7i}/k_{7c7}^{1/2})/\over /{ m mol^{1/2}}}$	$dm^{-3/2} s^{-1/2}$	$2.8 imes 10^{-5}$	$3.1 imes 10^{-5}$	4.0×10 ⁻⁵

than one order of magnitude less than the transition state estimate [12]. Assuming a tight transition state, FREY and WALSH [12] suggest 10^{10.5} s⁻¹ for the A-factor of 1,4-, 1,5- or 1,6-hydrogen shifts in free radicals. Accepting this value for A_{7i} and assuming $A_{7c7} = 10^{9.8}$ (the same as for ethyl recombination), we have $A_{7i}/A_{7c7}^{1/2} = 10^{5\cdot6} \text{ mol}^{1/2} \text{ dm}^{-3/2} \text{ s}^{-1/2}$ and obtain $E_{7i} - 1/2 E_{7c7} =$ $= 56.5 \text{ kJ mol}^{-1}$ from Eq. (41). These estimations show that the activation energies for n-alkyl radical isomerizations by 1,5-hydrogen shift are between 50 and 60 kJ mol⁻¹. A more accurate determination of the activation energy may be expected only from experiments carried out with a very clean radical source under conditions where the mechanism is simple and isomerization is the major reaction occurring.

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CORIOLIS COUPLING CONSTANTS AND CENTRIFUGAL DISTORTION CONSTANTS OF SOME TRIGONAL PYRAMIDAL XY₃ MOLECULES AND IONS

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With the help of kinetic constants, molecular constants, namely the Coriolis coupling constants and the centrifugal distortion constants of ten pyramidal XY_3 molecules have been evaluated. The values of these constants are reasonable and fall in the expected range, being also in good agreement with the observed values, which bears out the significance of the method of kinetic constants.

Introduction

Recently the attention of molecular spectroscopists has been attracted by the concept of kinetic constants. The kinetic constants of molecules and ions appear to be of basic significance in the study of the vibration of molecules and ions. Molecular kinetic constants are the vibrational inertial coefficients involved in WILSON'S expression for the kinetic energy relating to molecular vibrations, given by $2T = SG^{-1}S$ where $G^{-1} = K$. The utilization of kinetic constants in evaluating the molecular constants cannot be overemphasized. The determination of symmetry force constants involved in the secular equation from the n_i vibrational frequencies alone has been a mathematically underdetermined problem so far. Therefore any genuine attempt to evaluate all the symmetry force constants associated with a problem of order n > 1 should involve the incorporation of at least n_i $(n_i - 1)/2$ additional data other than the n_i frequencies. The method of kinetic constants seeks to relate the off-diagonal elements of the F matrix through the relation:

$$\frac{F_{ij}}{F_{jj}} = \frac{K_{ij}}{K_{jj}} [i < j: i, j = 1, 2]$$

WILSON'S F-G Matrix method, coupled with kinetic constants and redundancy constraints, has been found to lead to acceptable sets of molecular

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constants for several molecular types [1-8]. Extending this procedure to trigonal pyramidal XY₃ $[C_{3v}]$ molecules, the molecular kinetic constants, the potential constants and the mean amplitudes have been reported for group V hydrides and some halides [9].

The purpose of the present paper is to test the validity of the force field by calculating other molecular constants, *viz.*, Coriolis coupling constants and centrifugal distortion constants. The values obtained in the present investigation are in good agreement with the observed values, proving the significance of the procedure adopted.

Theoretical considerations

The kinetic constants, the potential constants, and the mean amplitudes of vibration of the $XY_3[C_{3v}]$ trigonal pyramidal type have already been reported [9]. Utilizing these force constants, the Coriolis coupling constants and centrifugal distortion constants are evaluated in the present work.

Coriolis coupling constants

The Coriolis coupling constants which can be determined experimentally, can also be evaluated from a reliable set of force constants and the values can be used for the detailed interpretation of vibrational spectra.

The Coriolis matrix elements $C_{ij}^{\alpha} [\alpha = x, y, z]$ are obtained by the vector method MEAL and POLO [10] and the zeta matrix elements are evaluated from the relation $\zeta^{\alpha} = L^{-1}C^{\alpha}(L^{-1})$ making use of the kinetic constants. The evaluated Coriolis coupling constants are given in Table I. The zeta values in Table I may be seem to obey the linear and quadratic sum rules given by OKA [11].

$$\begin{split} \zeta_{3a3b}^{z} \zeta_{4a4b}^{z} &- (\zeta_{3a4b}^{z})^{2} = -A \\ \zeta_{3a3b}^{z} + \zeta_{4ab4}^{z} &= A - 1 \\ (\zeta_{13a}^{y})^{2} + (\zeta_{14a}^{y})^{2} + (\zeta_{23a}^{y})^{2} + (\zeta_{24a}^{y})^{2} = (1/2)(A+1) \\ (\zeta_{3a4a}^{y})^{2} &= (1/2)(1-A) \end{split}$$

where $A = (I_{ZZ}/2I_{XX})$, I_{ZZ} is the principal moment of inertia about the z axis with respect to the center of mass.

$$\begin{aligned} & (\zeta_{13a}^{y})^{2} + (\zeta_{14a}^{y})^{2} + (\zeta_{23a}^{y})^{2} + (\zeta_{24a}^{y})^{2} + (\zeta_{3a4a}^{y})^{2} = 1 \\ & 2[(\zeta_{13a}^{y})^{2} + (\zeta_{14a}^{y})^{2} + (\zeta_{23a}^{y})^{2} + (\zeta_{24a}^{y})^{2} - 1/2] \\ & - (\zeta_{3a4b}^{z})^{2} + \zeta_{3a3b}^{z}(\zeta_{4a4b}^{z}) = 0 \end{aligned}$$

The zeta values also obey the relationship

 $\left(\zeta_{13a}^{\gamma}\right)\left(\zeta_{24a}^{\gamma}\right)-\left(\zeta_{14a}^{\gamma}\right)\left(\zeta_{23a}^{\gamma}\right)=0$

m-	1.1	-	т	
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Molecule	53a 3b - 54a 4b	53a 4b 	51 10 52 80	52 1a 53 ata
SbCl ₃	0.2519 (0.2586)	0.8014 (0.8141)	0.1294 (0.1085)	0.4896 (0.4799)
	0.4871 (0.4819)	0.2025 (0.2002)	0.7650 (0.7540)	$0.3432 \\ (0.3320)$
SbBr ₃	0.4225 (0.4418)	0.7465 (0.7752)	0.1965 (0.1613)	0.3969 (0.3976)
	0.6081 (0.5909)	0.3739 (0.3586)	0.7559 (0.7320)	0.3047 (0.2760)
${ m SbI}_3$	0.5480 (0.5587)	0.7111 (0.7282)	0.2202 (0.1829)	0.3385 (0.3336)
	0.6736 (0.6671)	0.4791 (0.4685)	0.7379 (0.7300)	0.2501 (0.2390)
BiCl ₃	0.1642 (0.1686)	0.8115 (0.8196)	0.0887 (0.0751)	0.5241 (0.5118)
	0.4341 (0.4341)	0.1271 (0.1277)	0.7521 (0.7510)	0.3674 (0.3600)
BiBr ₃	0.3071 (0.3145)	0.7970 (0.8063)	0.1501 (0.1268)	0.4691 (0.4572)
	0.5139 (0.5137)	0.2465 (0.2469)	0.7699 (0.7570)	0.3216 (0.3140)
BiI_3	0.4060 (0.4225)	0.7705 (0.7812)	0.1865 (0.1568)	0.4177 (0.4073)
	0.5806 (0.5788)	0.3437 (0.3412)	0.7679 (0.7350)	0.2870 (0.2820)
ClO ₃	0.3715	0.8363	0.1481	0.4829
	0.4901	0.2421	0.7920	0.2431
BrO ⁻ 3	0.2111	0.8834	0.0872	0.5609
	0.3556	0.1195	0.7689	0.2689
IO_3^-	0.1360	0.8522	0.0676	0.3614
	0.3610	0.0896	0.7484	0.3349
SeO ₃ ² -	0.1905	0.8105	0.1009	0.5154
	0.4481	0.1487	0.7571	0.3591

Coriolis coupling constants

Values in parantheses refer to values reported by TIMOSHININ et al.

 ζ_{3a3b}^z and ζ_{13a}^y are of the same order of magnitude except in the case of ClO_3^- and BrO_3^- . Uniform trends have been noticed in the Coriolis coupling constants for these cases. It can be seen from the table that the values of

 ζ_{4a4b}^z , ζ_{13a}^y , ζ_{14a}^y are uniquely negative in all cases. The higher value of ζ_{23a}^y indicates strong coupling between the two modes $v_2(A)$ and $v_3(E)$ in these cases. These constants are useful for band assignments, analysis of rotation structure and prediction of band shapes. The good agreement between the present results and the values obtained by TIMOSHININ *et al.* [12] underlines the significance of the method of kinetic constants.

Centrifugal distortion constants

The knowledge of centrifugal distortion constants are essential to determine the rotational energy levels of non rigid molecules. CYVIN *et al.* [13] have formulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of KIVELSON and WILSON [14, 15]. The quantities $t_{\alpha\beta\gamma\delta}$ have been obtained using CYVIN's relation and the non vanishing $T_{\alpha\beta,s}$ matrix elements have been evaluated. The centrifugal distortion constants of these six molecules and four ions have been calculated using the force constants given previously [9]. Table II deals with the evaluated centrifugal distortion constants of the molecules and ion under study. As expected, D_{JK} is negative in all the cases studied here. The centrifugal distortion constant calculated in this work for antimony trichloride agrees quite well with the observed values reported by CAZZOLI *et al.* [16], indicating the significance of the present method. The centrifugal distortion constants for other molecules are reasonable, falling in the expected

Molecule	D_J	$-D_{JK}$	D _K		
$SbCl_3$	0.5313 (0.5489)	0.7712 (0.7740)	0.3621		
$SbBr_3$	0.1148	0.1615	0.0795		
SbI_3	0.0333	0.0517	0.0239		
BiCl ₃	0.4790	0.5452	0.1872		
BiBr ₃	0.0622	0.0861	0.0392		
BiI ₃	0.0206	0.0298	0.0129		
ClO ₃	9.3491	14.8117	6.5195		
BrO ₃	5.8884	9.3556	4.2441		
IO ₃	3.6213	5.3654	2.4965		
$SeO_3^2 -$	3.8652	5.0951	2.2895		

Table II

Centrifugal distortion constants (kHz)

The data in parantheses are the observed values

range. Since, to our knowledge no experimental results are available for these cases to the corresponding constants evaluated in the present investigation are not compared.

Conclusion

On the whole, it is seen that the kinetic constants do play a fundamental role in molecular dynamics and their application to acceptable sets of molecular constants.

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DETERMINATION OF MICROGRAM AMOUNTS OF TANTALUM(V) WITH *p*-SULPHOBENZENEAZO--4-(2,3-DIHYDROXY-5-CHLOROPYRIDINE)

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The reagent p-sulphobenzeneazo-4-(2,3-dihydroxy-5-chloropyridine) reacts with tantalum(V) to form orange-red coloured solution with a maximum absorbance at 510 nm. The reaction is slow at room temperature (27 °C) and is complete in 10 min at 60 °C. The use of citric acid prevents the precipitation and hydrolysis of tantalum pentaoxide. The colour is stable for at least 16 hrs. The effects of heating temperature, time, pH, reagent concentration and other variables have been studied. The system follows the Beer's law over the concentration range investigated. The optimum condition range for measurement in 10 mm cell is $1-12 \,\mu g$ of tantalum(V). The molar absorptivity of the complex is 2.13×10^{6} L moles⁻¹ cm⁻¹. The metal-ligand ratio of 1 : 2 was found by spectrophotometric measurements and confirmed by Job's continuous variations and mole ratio methods.

Introduction

Several azo dyes as 1-(2-pyridylazo)-2-naphthol (PAN) [1]. 4-(2-pyridylazo)-resorcinol (PAR) [2] and eriochrome blue SE (3-[(5-chloro-2-hydroxyphenyl)azo]-4,5-dihydroxy-2,7-naphthalene disulphonic acid [3] *etc.* have reported to form complexes with tantalum(V). The present work deals with spectrophotometric investigation of tantalum — p-sulphobenzeneazo-4-(2,3--dihydroxy-5-chloropyridine) complex from analytical chemical aspects.

Experimental

Standard tantalum(V) solution (1 mg/mL)

Pure tantalum pentoxide (0.138 g) was fused with 10 g of potassium hydrogen sulphate in a silica crucible and after cooling the melt was extracted with 10 ml of 25% citric acid solution by warming. The solution was transferred in to a 100 ml standard flask. The pH was adjusted to about 4.0 with dilute ammonia and made up to the volume with double distilled water.

p-Sulphobenzeneazo-4-(2,3-dihydroxy-5-chloropyridine) solution

A solution (0.25% w/v) of the reagent was prepared in double distilled water.

Recommended procedure

To the tantalum solution (containing $25-300 \mu \text{g}$ of Ta) add 4-5 mL of 0.01 M solution of the reagent and adjust the pH to 5.5 by dilute ammonia. Heat the solution for about 10 min

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or allow to stand for 1 hr. Dilute it to 25 mL with distilled water. Measure the absorbance at 510 nm against the reagent blank prepared under the identical conditions and determine the amount of tantalum(V) using a calibration curve.

Results and Discussion

Spectral characteristics

The absorption maximum of the complex occures at 510 nm and there was no shift in the wavelength when either the pH was varied from 2.0 to 9.5 or the molar ratio of tantalum(V) to the reagent from 1:5 to 5:1. There-



Fig. 1. Absorption spectra of tantalum complex at various pH values. Ta(V) : $1.0 \times 10^{-5} M$; SDCP: $1.0 \times 10^{-4} M$. pH (1) 3.0; (2) 3.5; (3) 4.0; (4) 4.5; (5) 5.0; (6) 5.5; (7) 6.0

fore, all subsequent studies were carried out at 510 nm. In order to observe the spectral changes on varying the pH, absorption curves for tantalum complex were prepared at different pH values. The maximum absorbance of the tantalum complex was found at 510 nm at pH 5.5 and at shorter wavelength at lower pH.

Effect of hydrogen ion concentration

The influence of pH on the absorbance at 510 nm was studied over a pH range of 2.0-9.5. Maximum and constant absorbance was observed between pH 5.3 and 5.7. Therefore, pH 5.5 was conveniently adjusted for all further measurements.

SHARMA: DETERMINATION OF TANTALUM(V)

Calibration range, sensitivity and precision

A spectrophotometric method has been devised for the determination of microgram amounts of tantalum(V) using the reaction between p-sulphobenzeneazo-4-(2,3-dihydroxy-5-chloropyridine) and tantalum(\tilde{V}). The orangered coloured complex has its absorption maximum at 510 nm and pH 5.5 with molar absorptivity of 2.13×10^{-5} L mole⁻¹ cm⁻¹. The sensitivity is $4.30 \times$ $\times 10^{-4}$ µg tantalum(V) cm⁻¹ for log $I_0/I = 0.001$. The Beer's law is valid over the concentration range of 1-12 µg of tantalum(V) mL⁻¹. The precision of the method was evaluated by preparing and measuring 10 identical solutions containing 5 µg of tantalum solution. Standard deviation of the absorbance was 0.003.

Interference of foreign ions

Solutions containing 20 μ g of tantalum(V) and varying amounts of foreigns were prepared at pH 5.5 and tantalum was determined in their presence. The following ions with their amounts in μ g given in parenthesis did not cause more than $\pm 3\%$ deviation in the absorbance.

NO₃⁻ (350 µg), $C_2O_4^{2-}$ (300 µg), Cl^- (100 µg), Br^- (80 µg), F⁻ (60 µg), Al³⁺ (200 µg), Zn²⁺ (180 µg), Mn²⁺ (220 µg), Co²⁺ (140 µg), Pb²⁺ (120 µg), V(V) (300 µg), Nb(V) (150 µg), Mo(VI) (200 µg), U(VI) (320 µg), Po₄³⁻ (100 µg), Cr³⁺ (80 µg) and Fe³⁺ (60 µg).

Application of the method

Method

To determine tantalum spectrophotometrically in steels, dissolve 100 mg of sample containing 0.030 to 0.5% of tantalum in 50% sulphuric acid and heat until dense fumes appear. After cooling, add dilute hydrochloric acid and filter the silica and ignite. Add few drops of hydrofluoric acid and treat it with sulphuric acid. Fuse the residue with potassium pyrosulphate. Dissolve the solid and add to the main solution. Add 10 mL of *p*-sulphobenzenazo--4(2,3-dihydroxy-5-chloropyridine) solution and add 2% tannin solution drop by drop and stir until the precipitation of tantalum is complete. Filter the solution on filter paper (Whatman 41). Wash the precipitate with 1% tannin solution. Ignite the precipitate in a silica crucible and fuse the residue with potassium pyrosulphate, add 10 mL of 25% of citric acid solution to the cooled cake and add dilute ammonia to adjust the pH to 4.0. Transfer the

solution into a 100 mL flask, dilute to the mark with distilled water. Withdraw 5 mL solution in a 25 mL volumetric flask and add 10 mL of the reagent p-sulphobenzeneazo-4-(2,3-dihydroxy-5-chloropyridine) solution. Adjust the pH to 5.5 with dilute ammonia, and dilute to the volume with distilled water. After 1 hr measure the absorbance at 510 nm.

Application

The results of tantalum analysis in tantalum steels are given below

Samples	Tantalum % certified	Tantalum % found	
BCS — 261/1	0.066	0.065	
Jap — 655/2	0.030	0.025	

Stoichiometry of the complex

The stoichiometry of the complex determined with Job's method of continuous variation [4] and mole ratio method [5] was 1:2 tantalum(V)-p--sulphobenzeneazo-4-(2,3-dihydroxy-5-chloropyridine). The apparent stability constant evaluated by the mole ratio method was $\log K = 7.504 + 0.1$ at 27 °C.

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IR AND PMR STUDIES OF SOME URANYL--β-DIKETONE OXODONOR ADDUCTS

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Synergistic adducts of uranyl- β -diketones, such as those of thenoyl-trifluoroacetone (TTA) and benzoyltrifluoroacetone (BTFA) (X) with neutral oxodonors such as di-*n*-octylsulphoxide (DOSO), di-*n*-hexylsulphoxide (DHSO), di-*n*-butylsulphoxide (DBuSO), tri-*n*-butylphosphate (TBP), di-*n*-butyl-*n*-butylphosphonate (DBBP) and tri-*n*-butylphosphine oxide (TBPO) [L] were synthesised. Analytical data confirm their stoichiometry as UO₂X₂L. The infrared stretching frequencies (L-O, O-U-O, U-O) of these complexes and the bending frequency of the uranyl group $\delta(O-U-O)$ of the sulphoxide adducts measured at 270 MHz reveal the presence of a doublet of 6 line multiplets for the methylene protons of the sulphoxide group. The quartet observed for the α -methylene protons with phosphorus oxodonors has been shown to arise due to the overlap of two symmetrical triplets caused by adjacent methylene protons and ³¹P.The PMR spectra reveal the presence of a doublet for the γ -CH proton and additional shoulder peaks for TTA protons indicating at least two different electronic environments for TTA moieties in adducts with sulphoxides and tributylphosphine oxide but not with relatively weaker donors such as TBP and DBBP.

Introduction

In view of the importance of phosphorus oxodonors [1] and sulphoxides [2, 3, 4] as extractants for actinides, it was of interest to investigate further the synergistic adducts formed by them with uranyl- β -diketonates. Due to inherent disymmetry of the sulphur atom in sulphoxides, the two protons on the methylene group nearest to the sulphur atom are non-equivalent, although the non-equivalence is observed in the neat sulphoxides [5] only at high observing frequency (300 Mc). This non-equivalence is observed even at a lower frequency of 60 Mc in uranyl- β -diketone-sulphoxide adducts due to the shift reagent effect of the uranyl group [6]. Hence it was of interest to examine these complexes at a high observing frequency to see the effect on the α -methylene protons. It was also of interest to investigate the behaviour of α -methylene protons in phosphorus oxodonor adducts.

SIDDALL and STEWART [7] have reported the existence of similar complexes as a mixture of *cis-trans* isomers. Their evidence is based on the existence

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of the γ CH signal of TTA as a doublet and the appearance of additional shoulder peaks for the TTA ring protons. It was therefore of interest to examine if the complexes studied here also exist as *cis-trans* isomers.

Experimental

All the adducts were prepared by the usual procedure reported earlier [8, 9]. Their stoichiometry was ascertained as UO_2X_2L from elemental analysis for C, H and U and from molecular weight data.

Infrared spectra were measured in the range 4000-200 cm⁻¹ of samples as nujol mulls in CsI discs using a Perkin-Elmer 577 IR grating spectrophotometer and the characteristic peak positions reported in Table I. The PMR spectra of the sulphoxide adducts were measured at 270 MHz in CDCl₃ with TMS as internal standard using a Bruker 270 spectrometer and those of phosphorus oxodonor adducts at 60 MHz using Varian A60 spectrometer. The line positions and multiplicities are given in Table II.

Table I

Characteristic IR stretching frequencies (cm^{-1}) for free ligands and complexes

Cul etc.	L—0	0-U-0		U 0(V)		X0 U 0)	
Substance		asym	sym	0—0(X)	U-U(L)	0(0-0-0)	
UO ₂ (TTA) ₂ DOSO	960	913	865	498	355	256, 267	
DOSO	1002, 1020						
UO ₂ (TTA) ₂ DHSO	960	915	860	498	352 (w)	254, 266	
DHSO	1022, 1046					9	
UO2(TTA)2 DBuSO	962	917	862	498	349 (w)	252, 26	
DBuSO	1027					0	
UO ₂ (BTFA) ₂ DOSO	959	915	835	518	362	254, 279	
UO ₂ (BTFA) ₂ DHSO	957	920	836	518	362 (w)	254, 26	
UO2(BTFA)2 DBuSO	958	919	833	519	-	254, -	
UO ₂ (TTA) ₂ TBP	1208	929	-	498	-		
TBP	1260				•		
UO ₂ (TTA) ₂ DBBP	1168	925		495			
DBBP	1245						
UO ₂ (TTA) ₂ TBPO	1112	924	-	490	-	-	
TBPO	1145						

Results and Discussion

The analytical data of these complexes lead to their formulation as UO_2X_2L . The molecular weight measurements indicate them to be monomers in benzene.
Tabl	e	п		

PMR spectra of uranyl- β -diketone adducts with sulphoxides (270 MHz) and phosphorus oxodonors (60 MHz). Chemical shifts in δ ppm

Substance	αCH _z		TTA Protons		
	-	γСН	H(4)	H(5)	H(3)
UO ₂ (TTA) ₂ DBuSO	3.52(6), 3.24(6)	6.79(2)	7.28(4)	7.83(2), 7.80(Sh)	8.30(2), 8.15 (Sh)
UO2(TTA)2 DHSO	3.50(6), 3.24(6)	6.78(2)	7.30(4)	7.83(2), 7.80 (Sh)	8.25(2), 8.12 (Sh)
UO ₂ (TTA) ₂ DOSO	3.52(6), 3.24(6)	6.78(2)	7.29(4)	7.83(2), 7.80 (Sh)	8.25(2), 8.10 (Sh)
UO2(BTFA)2 DBuSO	_3.52(6), 3.24(6)	6.86(1)			
UO2(BTFA)2 DHSO	3.52(6), 3.24(6)	6.84(1)			
UO2(BTFA)2 DOSO	3.51(6), 3.24(6)	6.85(1)			
DBuSO	2.69(2)				
DHSO	2.67(12)				
DOSO	2.66(12)				
UO ₂ (TTA) ₂ TBP	4.47(4)	6.77(2)	7.18(2)	7.72(2)	8.02(2)
UO ₂ (TTA) ₂ DBBP	4.58(4)	6.88(2)	7.35(2)	7.88(2)	8.35(2)
UO2(TTA)2 TBPO	_	6.78(2)	7.27(2)	7.77(2), 7.52 (Sh)	8.27(2), 8.03 (Sh)
TBP	4.03(4)				
DBBP	3.98(4)				

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Infrared spectra

The O-U-O asymmetric stretching frequency has been observed as a strong band between 915 and 920 cm⁻¹ in the sulphoxide adducts and between 925 and 930 cm^{-1} in the phosphorus oxodonor adducts. A weak band observed in the region of 860-865 cm⁻¹ in the TTA complexes and 833-836 cm⁻¹ in the BTFA complexes with sulphoxide adducts has been attributed to the symmetric stretching frequency of the uranyl group. The decrease of S-Oand P-O stretching frequencies in the complexes from the value of the free ligands is indicative of bonding by oxygen of the donor. Shifts in the infrared stretching frequencies for P-O and S-O groups do not follow the order of co-ordinating abilities of the ligands due to significant contribution from varying degrees of $d\pi - p\pi$ interaction in different oxodonors. In the far-infrared spectra, U=0 (β -diketone) bands are observed at 500 cm⁻¹ for TTA complexes and at 520 cm^{-1} for BTFA complexes. Also a weaker band in the region of $350-360 \text{ cm}^{-1}$ has been correlated with the U-O (sulphoxide) stretching frequency. The higher value of the former compared to the latter indicates stronger bonding of the former. Bending frequency of the uranyl group, viz., $\delta(O-U-O)$ has been assigned to twin peaks in the region of 250-270 cm⁻¹ in sulphoxide adducts.

PMR spectra

a-Methylene protons: sulphoxide adducts

At 60 MHz, neat ligands (DBuSO, DHSO and DOSO) have been found to give only a triplet for the α -methylene protons corresponding to an A_2X_2 pattern. The non-equivalence of these protons is clearly seen at 270 MHz which gives 12 line multiplicity corresponding to an ABX₂ pattern in conformity with the presence of dissymmetry in the sulphoxide molecule. In the synergistic complex at 60 MHz, however, only 8 lines are observed (4 lines are invisible due to overlapping) which has been ascribed to the shift reagent effect of uranyl ion in these complexes [6]. When the spectra of the complexes are measured at 270 MHz, this effect is enhanced and two clear 6 line multiplets are observed (Fig. 1).

a-Methylene protons: phosphorus oxodonor adducts

Proton magnetic resonance of the α -methylene protons nearest to P-O bond of phosphorus oxodonors in these adducts occur in the region of 4.0 ppm (δ) as a quartet in the intensity ratio of 1:3:3:1 with a splitting of 6.5 c/s (Fig. 2). Since the nature of the quartet does not change on complexation though shifted downfield, it can be concluded that this does not arise due to the non-equivalence of the α -methylene protons as in the case of sulphoxides.



х - CH₂ — ТВР d-CH₂ — UO₂ (TTA)₂ ТВР

Fig. 2. PMR spectra at 60 MHz

In addition, as an analogy to sulphoxides, non-equivalence should result in a symmetrical triplet and not a quartet. This quartet can be shown to arise due to overlapping of two symmetrical triplets. α -Methylene protons are first split by the ³¹P(S = 1/2) nuclei into a doublet, each of which is further split

into two 1:2:1 triplets by the 2 protons on the adjacent methylene group. The overlapping of these two triplets results in a 1:3:3:1 quartet as observed. No such clear quartet is observed for TBPO adducts since the methylene protons are not sufficiently deshielded due to the absence of intervening oxygen atom and splitting due to ³¹P is very large. On complexation, the centre of the quartet shifts downfield more for DBBP (36 Hz) than for TBP (26 Hz) suggesting a stronger coordinating ability for the former.

β -Diketone protons

Four groups of signals are routinely observed for the TTA protons in those complexes. They are ascribed to the γ CH (doublet), H4 (quartet), H5 (doublet) and H3 (doublet) protons, respectively, in the order of decreasing shielding. SIDDALL and STEWART [7] have reported the appearance of shoulders to the main peaks in the complexes with TOPO which they ascribe to the existence of *cis-trans* isomers. However, in complexes with TBP and DMF, these additional shoulder peaks were observable only at low temperatures. Similar shoulders are also observed here for complexes with stronger donors such as TBPO and sulphoxides at room temperature which can be explained as due to the existence of these complexes as a mixture of *cis-trans* isomers. This is in conformity with the presence of a doublet for the γ CH proton in the TTA complexes.

Conclusion

Multiplets observed in the PMR spectra of the sulphoxide complexes have been ascribed to the presence of non-equivalent α -methylene protons caused by the dissymmetry of the S atom. Similar multiplets observed in TBP and DBBP complexes have been attributed to the spin coupling effect of ³¹P $(S = \frac{1}{2})$ nuclide. Coordinating ability of DBBP was found to be somewhat larger than that of TBP on the basis of complexation shifts in the multiplet centres of α -methylene protons in their respective complexes. PMR spectra of TTA protons in the synergistic complexes of sulphoxides and TBPO suggest the existence of these complexes as a mixture of *cis-trans* isomers.

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SOME PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF NiO-Sm₂O₃ BINARY SYSTEMS

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Several NiO samples with admixtures of $0.01-10.4 \text{ at.}_{0}^{\circ}$ Sm have been obtained. Chemical and phase compositions have been established. Specific surface area and contents of Ni³⁺ ions (total, lattice and surface) have been investigated. The measurements of catalytic activity in carbon monoxide oxidation have been performed within the temperature range of 393-638 K.

Introduction

Up till now, physico-chemical and catalytic properties of NiO-Sm₂O₃ systems have not been sufficiently investigated. Only a few papers deal with the interaction of NiO and Sm₂O₃ at high temperatures. According to some authors [1,2,3], no products of synthesis of these two oxides come into being during sintering up to 1673 K. DEMAZEAU *et al.* [4] have obtained SmNiO₃ of the structure of deformed perovskite by heating a mixture of NiO and Sm₂O₃ in the presence of KClO₃ at 1223 K, under an oxygen pressure of 6×10^6 Nm⁻². TAKASU and coworkers [5] have investigated the catalytic activity of NiO-Sm₂O₃ systems, containing Sm₂O₃ up to 20 mol %, in the reaction of NO oxidation.

The present paper is a part of our studies of NiO-rare earth oxide systems and deals with the influence of varying amounts of Sm_2O_3 on the quantity of Ni³⁺ in NiO and on some other physico-chemical properties and the catalytic activity in CO oxidation.

Experimental

NiO samples with admixtures of 0.01-10.4 at.% of Sm were obtained by coprecipitation of basic nickel(II) and samarium(III) carbonates from a solution of nitrates with a saturated solution of ammonium carbonate. Nitrate-free precipitates were dried at room temperature, crushed and calcined for 2 h at 673 K and then for 6 h at 1273 K in air atmosphere. A screen fraction of 0.06-0.12 mm was used for all the measurements. Nickel in the samples was determined electrolytically; after its separation, samarium was determined by titration with EDTA in the presence of xylenol orange as an indicator. Diffractometer analysis was

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performed using Cu K α and Co K α radiations. The specific surface area was measured using the dynamic BET method, applying low-temperature nitrogen adsorption. The total amount of Ni^{3+} ions and their contents in the lattice were estimated by our method reported earlier [6]. The quantity of Ni^{3+} ions per unit surface area was calculated from the equation

$$X = \frac{A_{\text{total}} - A_{\text{lattice}}}{S}$$

where: A_{total} — the total amount of Ni³⁺ ions, A_{lattice} — lattice Ni³⁺ ions, S — specific surface area.

The catalytic activity in CO oxidation was measured by a flow method using a Pyrex microreactor within the temperature range of 393-638 K. Reaction products were analyzed chromatographically. 0.1 g of the catalysts with a dispersity of 0.06 - 0.12 mm was mixed with quartz powder having the same grain size and then put into the reactor over a layer of quartz wool. The catalyst bed was covered with 2 cm³ of quartz powder. Volume composition of the reactant gas was: $CO: O_2 = 4:3$, and its total velocity 0.49 cm³s⁻¹. The time of reaction was 45 min at each temperature. Before catalytic measurements the catalysts were outgassed for 1 h in a stream of argon at 683 K. Specific catalytic activities were calculated from the equation

$$A_{\rm STP} = \frac{X \cdot V_{\rm STP}}{S \cdot W}$$

where: X — degree of conversion of CO, V_{STP} — volume velocity of CO under standard conditions, mmole s⁻¹, W — weight of catalyst, g, S — specific surface area, m²g⁻¹.

Results and Discussion

In our investigations we employed a series of NiO samples with various samarium admixtures calcined at 1273 K and for comparison with pure oxides of nickel and samarium. Calcination at 1273 K (about 200 K higher then TAMMAN's temperature for NiO [7, 8]) facilitated the diffusion of Ni²⁺ and Sm^{3+} and rendered it possible to establish the equilibrium between nickel(II) oxide and the surrounding atmosphere.

Pure NiO was green and the samples became more grey with an increase of Sm₂O₃ admixture.

Contents of samarium in the preparations are given in Table I. The measured values are larger than expected; this was caused by the fact that under the preparation conditions (pH = 7.0) all the Sm³⁺ ions were precipitated and a small part of Ni²⁺ ions were still in solution. This is due to the possibility of formation of amminenickel(II) complexes.

X-ray analysis performed for samples S-7, S-9, N-0, S-0 and those of Sm₂O₃ doped with 5, 10 and 15 at.% Ni shows only lines of NiO and Sm₂O₃. There exist no lines connected to any new phase which could originate from the interaction between NiO and Sm₂O₃ at the high temperature. These results confirm that the investigated samples consist of two different phases: NiO and Sm_2O_3 and (as opposed to NiO doped with Dy_2O_3 and Ho_2O_3) the X-ray

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No.	Composition	Specific surface area (m ² g ⁻¹)
N-0	NiO	0.23
S-1	NiO + 0.01% at. Sm*	0.40
S-2	NiO $+$ 0.02% at. Sm*	0.63
S-3	NiO $+$ 0.05% at. Sm*	0.78
S-4	NiO $+$ 0.14% at. Sm	0.71
S-5	m NiO+~0.24% at. Sm	1.08
S-6	NiO + 0.53% at. Sm	2.33
S-7	m NiO+~1.00% at. Sm	2.92
S-8	NiO $+$ 3.20% at. Sm	3.75
S-9	NiO + 5.00% at. Sm	3.90
S-10	NiO + 7.30% at. Sm	4.16
S-11	NiO + 10.40% at. Sm	3.23
S-0	Sm_2O_3	1.17

Table I

Sample compositions and specific surface areas

* The precise samarium content has not been measured

lines of NiO are not shifted. We observed, however, a displacement of some lines of Sm_2O_3 to larger angles (smaller values of the lattice parameter). An additional X-ray analysis was performed (range of angles $15-20^{\circ}$, small velocity of the X-ray-meter, $0.008^{\circ} s^{-1}$) using the following preparations: S-11 (a), Sm_2O_3 doped with 5.0 at.% Ni (b) pure Sm_2O_3 (c) and (a) and (b) mixed with pure Sm_2O_3 in the amount corresponding to its contents in these samples (see Table II). The data of this Table show that in the case of sample (a) one of the *d*-values (0.3194 nm) decreased by 0.0012 nm as compared with that of pure Sm_2O_3 . For sample (b) this value is only 0.0006 nm lower than for Sm_2O_3 . The same *d*-values for (a) and (b) with admixtures of Sm_2O_3 are smaller only by 0.0003 and 0.0004 nm, respectively. Changes of the relative intensities of X-ray lines were also observed, mainly in the X-ray spectrum of (b). This seems to indicate some deformation of the coordination polyhedron in samarium oxide, which is probably due to the incorporation of a certain amount of Ni²⁺ ions (or Ni³⁺ ions) into its crystal lattice.

As seen from Table I the specific surface area of the samples increases rapidly along with the rise of amounts of the dopant and reaches a maximum for sample S-10. This phenomenon can be attributed to retardation of the sintering process due to the admixture of the foreign phase [9]. The influence of calcination temperature on the defectation of NiO crystal lattice is well known from the literature [10-14]. An enhanced sintering of NiO following the rise of the heating temperature results in a decrease in nickel vacancies

Table II

S-11 (a)		S-11 mixe with Sm ₂	d O ₃	Sm ₂ O ₃ + 5 (b)	5% Ni	$Sm_2O_3 + Sm_2O_3 + Sm_2O_3$	5% Ni rith s	Sm ₂ O ₃ (c)	
đ (nm)	I/I。 (%)	đ (nm)	I/Ia (%)	đ (nm)	I/I。 (%)	d (nm)	I/I ₀ (%)	đ (nm)	I/I。 (%)
0.3200	95	0.3202	100	0.3194	54	0.3203	72	0.3206	96
0.3057	92	0.3058	83	0.3059	100	0.3059	100	0.3059	89
0.3984	96	0.2986	92	0.2990	55	0.3990	86	0.2990	99
0.2903	60	0.2903	61	0.2903	43	0.3903	54	0.2903	58
0.2858	92	0.2858	91	0.2858	72	0.2858	84	0.2858	93
0.2792	100	0.2792	100	0.2792	38	0.2792	65	0.2792	100

Results of diffractometer analysis performed using Co K α radiation. Range of angles 15–20°, velocity of X-ray counter 0.008° s⁻¹

and a reduction of some Ni³⁺ ions. In the case of our samples, the growth of the quantity of Ni³⁺ ions in the crystal lattice together with the growth of samarium contents up to about 1 at.⁰/₀ (Fig. 1A, curve 2) additionally confirm



Fig. 1. (A): Total (1) and lattice (2) amounts of Ni³⁺ ions, (B): Quantity of Ni³⁺ ions per 1 m² of the surface, (C): Degree of CO conversion vs. samarium concentration

T	a	bl	e	П	Т	
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No.	Temp. Agrp	393 K ×104	443 K ×104	$\begin{array}{c} 493 \text{ K} \\ \times 10^3 \end{array}$	$543 \mathrm{K} \times 10^3$	593 K ×10 ²	$638 \mathrm{K} \times 10^2$
N-0						0.76	1.20
S-1					2.89	1.81	18.20
S-2					1.82	1.09	10.90
S-3					2.57	2.74	10.40
S-4				3.08	6.80	1.62	4.63
S-5			11.70	3.94	7.99	1.91	4.04
S-6			6.41	2.27	5.72	1.23	2.58
S-7		3.93	7.08	2.68	4.80	1.00	2.21
S-8		3.68	8.89	2.21	6.26	1.27	2.20
S-9		2.65	7.96	2.59	5.34	1.20	2.35
S-10		1.93	6.35	1.96	4.15	0.88	1.39
5-11			6.05	1.49	3.81	0.68	1.51
5-0							0.12

Specific activity A_{STP} mmol CO m⁻² s⁻¹ in the reaction of CO oxidation at different temperatures

the effect of Sm₂O₃ phase on the retardation of the sintering process. Since most of the Ni³⁺ ions exist on the surface of NiO due to the chemisorption of oxygen [15, 16], the total amount of Ni³⁺ increases with a rise of specific surface area. However, the changes are not quite parallel because of the lowering the Ni³⁺ content per unit surface area. We can state here that the decrease of oxygen coverage depends both on the diminishing of the chemisorption of oxygen (acceptor gas) with a growth of defectation of NiO [17] and on the "blocking" of the NiO surface by the Sm₂O₃ phase. Figure 1C is a plot of CO conversion (over 0.1 g catalysts) vs. samarium concentration. Pure oxides of nickel and samarium show very slight activity as catalysts for the oxidation of CO to CO₂; the conversions were very small even at the highest temperatures used. Under the same conditions the doped samples are very active as catalysts and their activity increases with increasing temperature. One should distinguish, however, two groups of samples, 0.01-0.05 at.% Sm and 0.14-10.4at.% Sm, which are very different in their catalytic behaviour. Preparations with small amounts of admixture are only slightly active at lower temperatures, up to 593 K. At 638 K they show very high activity, similar to that of the most active catalysts (Fig. 1C) in spite of their much smaller specific surface areas $(0.40 \text{ m}^2 \text{g}^{-1} \text{ for S-1}, 3.75 \text{ m}^2 \text{g}^{-1} \text{ for S-9}).$

As is seen from Table III, the doped samples show higher specific activity than pure NiO. The specific activity of S-1-S-3 is very low in the range of 543-593 K; at 638 K their activity is much higher than that of other

preparations. We can state here that, apart from samples S-1-S-3 at 543 and 593 K, the specific activity in CO conversion decreases with increasing samarium content in the catalyst.

The above mentioned increase in the rate of CO conversion (catalytic activity) in the case of doped samples as compared with pure NiO can be attributed to the increase of the defectation of NiO caused by the incorporated admixture. This phenomenon is well known from the literature. BIELAŃSKI and co-workers [18] have observed that the growth of NiO activity is caused by the increase of the quantity at Ni³⁺ ions due to lithium ion incorporation. Other authors [19, 20] have also observed the increase of NiO activity in this reaction after introducing acceptor impurities and lowering the activity caused by the decrease of NiO nonstoichiometry, which in turn, is due to admixtures of the donor type (e.g. Fe^{3+} , Cr^{3+}). On the other hand, since pure Sm_2O_3 is quite inactive as a catalyst in the temperature range in which we have studied the decrease of the specific activity of the doped samples (very low CO conversion only at 683 K), can be the result of the above mentioned "blocking" of the NiO surface by the inactive Sm_2O_3 phase, especially in the case of samples with more admixtures (above 0.05 at.% Sm). We can also expect, in accordance to TANABE's hypothesis [21], some modifications of the catalyst surface resulting from the formation of a surface solution of Sm_2O_3 in NiO, and also some changes in the activity of the catalysts. To sum up, we can state that Sm_2O_3 plays the role of the promoter in the investigated systems. The Sm^{3+} ions do not act as donor impurities (as e.g. Cr^{3+} and Ga^{3+}), which lower the nonstoichiometry of NiO. On the contrary, because of the retardation of the process of sintering, the amount of lattice Ni³⁺ ions strongly increases as does the specific surface area. These two factors make changes in the catalytic activity in the conversion of CO with oxygen very advantageous.

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DETERMINATION OF LEAD IN OILS BY ATOMIC ABSORPTION SPECTROMETRY USING A MODIFIED DELVES CUP TECHNIQUE

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The determination of lead in oils with a Modified DELVES Cup technique made of quartz as heat resistant material is described. Accurate results can be obtained on 10 mg of sample, with sample pretreatment consisting of dilution.

The accuracy of the method has been established by comparison with the colorimetric method.

Recently several atomic absorption methods utilizing various microsampling techniques have been described. The sampling boat system [1, 2, 3]and the DELVES Cup method [4] and its modified versions [5-11] are attractive because of the improved sensitivity obtained so that only a small sample is required for analysis. The DELVES Cup method offers great possibilities: it accepts small volumes of samples, it is rapid and does not require a great degree of technical competence. The procedure involves the atomization of metal from a cup into an absorption tube over an air-acetylene flame. The absorption signal is recorded and consists of peaks.

The technique is limited to elements which are easily atomized (for example Pb, Cd, Hg, Se, Ag, As). Determination of lead is becoming increasingly important both for toxicology and industrial screening.

The determination of lead in blood, urine and organic materials measured by AAS using the DELVES Cup technique is well known and has been studied [4-11].

The present study was undertaken to improve the method developed by **DELVES** for lead analysis in oils (vegetable oils, lubricant oils, *etc.*). The principal differences between the present modification and the original **DELVES** method is in the material of the system using quartz and sample preparation. Besides, it tries to use the method for the determination of lead content in new type of samples, oils.

Experimental

The absorption tube and cup made of some heat resistant material (quartz) is placed directly into the flame (100 mm $\log \times 15$ mm o.d. with a 8 mm diameter entrance hole). The flame heats the tube, atomizing the sample very quickly (without any loss of sample). The position of the tube is adjustable in all three dimensions.

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Fig. 1. Absorption signals at 283.3 nm

If the sample is allowed directly to enter the flame considerable smoke is given off and produces an apparent absorption signal. By using a fast recorder (chart speed 50 mm/min), the lead atomic absorption signal can easily be resolved from the non-specific absorption signal of smoke. We have no background corrections to remove the effects of the non-specific absorption signal.

It is, therefore, neccessary to char the sample until no more visible smoke appears. One way to dry the sample is to bring the cup containing the sample into a furnace at a temperature not higher than 500 °C [12].

Samples of different viscosity are prepared with MIBK (about 20 mg oil sample is diluted with MIBK to 100 μ L). A 10 μ L volume of the sample after preparation is measured directly into the cup. The sample in the cup is placed into the open furnace, preheated and set at 500 °C. The sample is continuously dried, charred and finally ashed (3-5 min). The cup with the ash is placed into a holder of the atomic absorption spectrophotometer and pushed to the center of the burner. An air-acetylene flame is allowed to burn with the tube for at least 5 min to allow the atomization system to come thermal equilibrium.

The response is fast, the curve reaches its peak and returns to the baseline after about 4 sec (Fig. 1).

To compensate for matrix interferences, it is necessary to standardize the analytical technique by the method of addition.

Standardization and measurement of the linear range of the calibration curve are accomplished by the addition of solution of known lead concentration to a sample with about 0.10 μ g/g lead. The calibration curve is shown in Fig. 2.



Fig. 2. Analytical curve showing additions of lead samples

Recommended Procedure

About 10–10 mg unknown and known lead samples are measured and diluted with MIBK to 100 μ L and 10 μ L of the prepared sample is placed into the cup.

The concentration of lead in the sample is given by

$$Sample \text{ conc.} = Standard \text{ conc.} imes rac{ ext{peak height for sample}}{ ext{peak height for standard}}$$

Lead contents of lubricating oils and vegetable oils are shown in Table I, determined by the modified DELVES Cup Technique and spectrophotometric method [13]. Operating conditions for the determination of lead in oils are shown in Table I.

To test the reproducibility of the analysis, two samples were run ten times. The data are shown in Table II.

The modified DELVES Cup technique described in this paper can be recommended, after checking for determination of other suitable metals in other substances, too.

Table I

Sample		AAS Modified DELVES Cup Method (µg/g)	Spectrophotometric determination [13] (µg/g)	
Vegetable oil	1	0.19	0.21	
	2	0.36	0.33	
	3	0.21	0.20	
Lubricating oil	4	0.13	0.12	
	5	0.68	0.74	
	6	0.82	0.85	

Comparison of results for lead in oil samples

wavelength (nm)	283.3
lamp current (mA)	4
slit width (nm)	0.04
scale expansion	$8 \times$

burner: acetylene slot burner, 100 mm/L slot non-luminous air-acetylene flame,

acetylene flow 4 dm³ min⁻¹

air flow 20 dm³ min⁻¹

recorder chart speed: 50 mm min⁻¹

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Table II

Reproducibility of lead content in oil samples by the modified DELVES cup method

Sample	$rac{\mathrm{Mean}\pm\mathrm{SD}}{(\mu\mathrm{g/g})}$
1	0.36 ± 0.04
2	0.68 ± 0.06

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PREPARATION AND STUDY OF CHELATING RESINS, IV

DETERMINATION OF THE PROTONATION CONSTANTS OF A CHELATING RESIN CONTAINING ETHYLENEDIAMINE FUNCTIONAL GROUPS

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The determination of the protonation constants of immobilized ethylenediamine is described. For the calculation the following equation was used:

$$\sum_{j=0}^{\mathbf{N}} \left\{ \beta'_{j} (\mathbf{H}^{+})^{j} \left[\bar{\alpha}^{*} - N + j \right] \right\} = 0$$

This relationship was derived earlier and has also been applied to calculate the protonation constants of polycarboxylate groups bound covalently to an insoluble resin phase.

The following values were obtained for the logarithm of the protonation constants at 298 K and at an ionic strength of 1 mol dm^{-3} :

$$\log K_1 = 9.77 \pm 0.09$$

 $\log K_2 = 7.12 \pm 0.10$

Introduction

In previous paper [1] a general equation was derived for the calculation of the protonation constants of immobilized bases. The equation was used for the estimation of the protonation constants of the polyethylene-polyaminopolycarboxylate groups bound to an insoluble polymer matrix. The following functional groups were studied [2, 3] diethylenetriaminetetraacetic acid, ethylenediaminetriacetic acid and iminodiacetic acid. Chelating resins containing the last two groups are sold by the Reanal Fine Chemical Factory (Budapest) under the trade name Ligandex-E and Ligandex-I.

This paper is concerned with the determination of the protonation constants of a resin containing ethylenediamine functional groups (ED-resin).

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Theoretical

The protonation steps of immobilized ethylenediamine (R-ED) can be represented by the following equations:

$$\overline{\mathbf{R}-\mathbf{E}\mathbf{D}} + \mathbf{H}^{+} + \mathbf{G}^{-} \rightleftharpoons \overline{\mathbf{R}-\mathbf{H}\mathbf{E}\mathbf{D}}^{+} + \overline{\mathbf{G}^{-}}$$
(1)

$$\overline{\mathbf{R} - \mathrm{HED}}^{+} + \mathrm{H}^{+} + \mathrm{G}^{-} \rightleftharpoons \overline{\mathbf{R} - \mathrm{H}_{2}\mathrm{ED}}^{2} + \overline{\mathrm{G}}^{-}$$
(2)

(bars are used to indicate components in the resin phase).

For the interpretation of the above protonation processes the following definition were introduced [1]:

1. The resin phase is considered as a concentrated electrolyte solution containing the following species:

- the immobilized base, R-ED,
- the protonated forms of the base, R-HED+ and R-H₂ED²⁺,

- counter ions, G⁻, and

- water, H₂O.

2. For the calculation of the overall protonation constants (β'_j) the following equation was used:

$$\sum_{j=0}^{1} \{\beta'_{j} (\mathbf{H}^{+})^{j} \left[\bar{\alpha}^{*} - N + j \right] \} = 0$$
(3)

where:

- $\bar{\alpha}^*$ is the degree of titration when the fully protonated base is titrated with a strong base, see also Eq. (9);
- N is the total number of protons that can be bound to one mol of the immobilized base (in our case N = 2);
- (H+) is the equilibrium hydrogen ion activity of the resin phase, see also Eqs (5) and (8).

In this paper, parentheses always represent concentrations in the resin phase in terms of mmol/(g water in the resin); barred symbols mean amount of substance in the resin phase in terms of mmol/(g dry resin containing the functional group in non-protonated form).

3. Due to the lack of the $\overline{\gamma}_{G}$ term the equilibrium hydrogen ion activity of the resin phase was estimated from the following equation:

$$(\mathbf{H}^{+}) = a_{\mathbf{H}} \left[\frac{(\mathbf{G})}{a_{\mathbf{G}}} \right]^{\pm 1}$$
(4)

The sign of the exponent in Eq. (4) corresponds to the sign of the counter ion, which is negative in this case, therefore:

$$(\mathrm{H^+}) = a_\mathrm{H} \frac{a_\mathrm{H}}{(\mathrm{G})} \tag{5}$$

 $\overline{\gamma}_{G}$ is included in K' values, see Eqs (11), (12) and (13).

In Eqs. (4) and (5)

$a_{\rm H}$ and $a_{\rm O}$ are the hydrogen ion and the counter ion activities, respectively, in the solution phase,

(G) is the concentration of the counter ions (chloride) in the resin phase. The counter ions may originate from two sources:

a) Counter ions compensating the charges of the immobilized components. This amount of counter ions will be referred to as chemically bound counter ions, $\overline{G_{\text{chem}}}$. In the case of the ED-resin studied, its amount should exactly be equal to the amount of the protons in the resin:

$$\overline{\text{Cl}_{\text{chem}}} = \overline{\text{R} - \text{HED}}^{+} + 2 \cdot \overline{\text{R} - \text{H}_2 \text{ED}}^{2+}$$
(6)

b) Counter ions invading thorugh the distribution of the electrolyte used to adjust the ionic strength in the solution, $\overline{\text{Cl}_{inv}}$.

The total concentration of the counter ions in the resin phase:

$$(\mathbf{G}) = (\mathbf{Cl}^{-}) = \frac{\overline{\mathbf{Cl}_{chem}} + \overline{\mathbf{Cl}_{inv}}}{\overline{\mathbf{H}_2 \mathbf{O}}}$$
(7)

On the basis of Eq. (5), the pH in the resin phase is given as:

$$\overline{\mathbf{pH}} = -\log\left(\mathbf{H}^{+}\right) = \mathbf{pH} + \log\frac{(\mathbf{Cl}^{-})}{a_{\mathbf{Cl}}}$$
(8)

4. The degree of titration, $\overline{\alpha}^*$, for this case can be expressed as:

$$\overline{\alpha}^* = N - \frac{\overline{\mathbf{G}_{\text{chem}}}}{Q} + \frac{(\mathbf{H}^+) - (\mathbf{OH}^-)}{Q/\overline{\mathbf{H}_2\mathbf{O}}}$$
(9)

where Q is the capacity of the resin in mmol/g ED-resin.

If Eq. (3) is used for the calculation of the constants of the ED-resin, then the following equation is obtained:

$$\frac{2 - \overline{\alpha}^*}{(\overline{\alpha}^* - 1)(\mathbf{H}^+)} = K_1' + \frac{\overline{\alpha}^*(\mathbf{H}^+)}{\overline{\alpha}^* - 1} \cdot K_1' K_2'$$
(10)

where

$$K'_1 = \frac{K_1}{K_{\bar{\nu}1}}$$
 and $K'_2 = \frac{K_2}{K_{\bar{\nu}2}}$ (11)

In the $K_{\overline{\nu}_1}$ and $K_{\overline{\nu}_2}$ terms, the activity coefficients of the immobilized components are lumped together:

$$K_{\bar{\gamma}1} = \frac{\bar{\gamma}_{\mathsf{R}-\mathsf{HED}} \cdot \bar{\gamma}_{\mathsf{G}}}{\bar{\gamma}_{\mathsf{R}-\mathsf{ED}}}$$
(12)

$$K_{\overline{\gamma}2} = \frac{\overline{\gamma}_{\mathsf{R}-\mathsf{H}_{*}\mathsf{ED}} \cdot \overline{\gamma}_{\mathsf{G}}}{\overline{\gamma}_{\mathsf{R}-\mathsf{H}\mathsf{ED}}}$$
(13)

 K_1 and K_2 are the thermodynamic equilibrium constants for the protonation reaction of Eqs (1) and (2).

From experimental data (pH, Cl_{chem}, Cl_{inv} and H₂O), the corresponding values of $\overline{\alpha}^*$ and (H⁺) can be calculated, and from these, K'_1 and K'_2 can be obtained by the above equation.

Experimental

The ED-resin was synthesized earlier and its properties have been described in ref. [4]. The resin studied was washed with 1 mol dm⁻³ hydrochloric acid and then treated with 0.1 mol dm⁻³ hydrochloric acid, whereby the protonated form of the base (R-H₂ED²⁺ \cdot 2 Cl⁻) was obtained. The air-dried protonated resin was stored in a desiccator in a glass-stoppered flask.

Titration curve of the resin

Approximately 0.5 g resin samples were weighed accurately into 100 cm³ glassstoppered flasks and to them increasing volumes of 0.1 mol dm⁻³ carbonate free potassium hydroxide solution were added. The ionic strength and the 100 cm³ final volume of the suspension was adjusted by the addition of a calculated volume of water and potassium chloride solution of 2 mol dm⁻³. The pH-metric titration curve was obtained at an ionic strength of 1 mol dm⁻³. The suspensions were left to equilibrate at 298 K for about 10 days.

The preparation and the equilibration of the samples as well as the determination of the pH were made in a protecting argon atmosphere.

Measurement of the quantities used to calculate $\overline{\alpha}^*$ and (H⁺)

The pH's of the equilibrium systems were measured by a calibrated glass electrode (Radiometer GK 2351 B) using a Radiometer PHM 64 Reasearch pH Meter.

After the measurement of the pH the solution phase was separated from the resin by filtration and by centrifugation (at 5000 r.p.m. for 30 min). The water content, $\overline{H_2O}$, was obtained by drying the resin in a protecting argon atmosphere at 378 K. The chloride content, $\overline{\text{Cl}_{\text{chem}}} + \overline{\text{Cl}_{\text{inv}}}$, of the dried resin was eluted into a 500 cm³ graduated flask with 100 cm³ of 0.1 mol dm⁻³ carbonate free potassium hydroxide solution. The resin was then washed free of base with carbonate free water, and finally the flask was made up to the mark.

The total amount of chloride ions originating from the two sources was obtained by potentiometric titration in 50 vol. % methanol using silver nitrate solution as titrant. The amount of chemically bound chloride was obtained from an acid-base titration

of the eluent solution.

Fure 1 shows the chemically bound chloride as a function of the added amount of potassium hydroxide.

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Fig. 1. Amount of chemically bound chloride ions as a function of the amount of potassium hydroxide added

The amount of the invading chloride was calculated from the above data:

$$\overline{\mathrm{Cl}_{\mathrm{inv}}} = \overline{\mathrm{Cl}} - \overline{\mathrm{Cl}_{\mathrm{chem}}}$$
(14)

Finally the eluted resin was dried overnight in a protecting argon atmosphere at 378 K to determine the mass of non-protonated resin.

The capacity of the resin was obtained as one half of the maximum aomunt of the chemically bound chloride and it was found as follows:

$$Q = 4.3 \frac{\text{mmol functional groups}}{\text{g ED-resin}}$$

Exactly the same capacity value was obtained through the determination of the nitrog gen content of the resin (by the method of KJELDAHL).

Figure 2 shows the titration curve of the ED-resin constructed using the correspondinpH and $\bar{\alpha}^*$ values of Table I.



Fig. 2. Titration curve of ED-resin

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Experimental data and details for the calculation of protonation constants of ED-resin

рН	Cl _{chem}	Clinv	$\overline{\mathrm{H_2O}}$	(C1-)	pH	ā*	mmol KOH mmol functional group
5.175	8.080	1.086	1.954	4.690	6.062	0.121	0.13
5.902	7.167	0.891	1.796	4.486	6.769	0.333	0.33
6.057	7.054	0.682	1.707	4.531	6.929	0.360	0.36
6.187	6.565	0.820	1.664	4.438	7.050	0.473	0.47
6.343	6.230	1.065	1.625	4.489	7.211	0.551	0.54
6.476	5.861	0.962	1.568	4.351	7.330	0.637	0.61
6.636	5.574	1.023	1.524	4.328	7.488	0.704	0.67
7.065	4.869	0.726	1.399	3.998	7.882	0.868	0.87
7.439	4.367	0.634	1.308	3.822	8.237	0.984	1.01
7.922	3.693	0.669	1.225	3.560	8.689	1.141	1.15
8.504	2.937	0.860	1.140	3.332	9.242	J.317	1.27
8.612	2.771	0.715	1.076	3.239	9.338	1.356	1.35
8.899	2.373	0.601	0.994	2.991	9.590	1.448	1.43
9.196	2.032	0.491	0.950	2.654	9.835	1.527	1.55
9.338	1.819	0.464	0.901	2.532	9.957	1.577	1.61
9.512	1.563	0.504	0.914	2.263	10.082	1.636	1.68
9.728	1.254	0.444	0.842	2.015	10.248	J.708	1.76
10.121	0.830	0.494	0.841	1.573	10.533	1.807	1.88
10.652	0.398	0.573	0.841	1.155	10.930	1.907	2.02
11.561	0	0.727	0.959	0.757	-		2.36
11.863	0	0.677	0.943	0.718	_	_	2.64
12.243	0	0.655	0.923	0.710	_		3.40
12.782	0	0.561	0.875	0.642	_	—	6.80
			1				

For details and units see text

Results and Discussion

Interpretation of chloride and water uptake

As can be seen in Fig. 1, the amount of chemically bound chloride gradually decreases as the amount of potassium hydroxide increases. The decrease of the $\underline{H}Cl$ content of the resin is equivalent to the added amount of potassium hydroxide but a small deviation occurs in the lower range of the chloride content. This small deviation can be explained if the swelling behaviour of the resin is taken into consideration.

In Fig. 3, the volume change of the resin bed is shown as a function of the solution. As the curve shows, the volume of the deprotonated resin is

about one half of the volume of the fully protonated one. At high pH values the resin strongly shrinks and consequently the desorption process of the ions is more hindered than at the lower pH.

The volume change, accompanying the protonation process obviously manifests itself in the change of the water content of the resin, which is represented in Fig. 4 as a function of the amount of added potassium hydroxide.



Fig. 3. Change of the volume of ED-resin as a function of the pH



Fig. 4. Change of the water content of the ED-resin as a function of potassium hydroxid added

When the functional groups are completely deprotonated the resin phase contains only the invading electrolyte. The concentration of the invading electrolyte was found to be about 0.7 mol dm⁻³ when the resin was in equilibrium with an external solution of 1 mol dm⁻³.

The initial period of protonation is not accompanied by a significant change in the water content, but in subsequent periods, it is increasing proportionally with the advance of protonation. From that proportional range one finds that together with the bonding of 1 mol HCl, about 9 mol H_2O is transferred simultaneously into the resin phase.

Calculation of the protonation constants

The data necessary for the calculations are given in Table I. By Eq. (10), the K'_1 and K'_2 were calculated from the falling in the $0.2 < \overline{\alpha}^* < 0.8$ and $1.2 < \overline{\alpha}^* < 1.8$ ranges. Equation (10) gives a linear relationship between $\overline{\alpha}^*(\mathbf{H}^+) = \overline{\alpha}^* = 1$ and $\frac{2 - \overline{\alpha}^*}{(\overline{\alpha}^* - 1)(\mathbf{H}^+)}$ and the intercept of the straight line gives K'_1 , whereas from its slope K'_2 can be calculated.

The following values were obtained:

$$\log K_1' = 9.77 \pm 0.09$$

 $\log K_2' = 7.12 \pm 0.10$

The uncertainty intervals associated with all values are given as three times the standard deviation.

In the literature on the equilibria of polyacids, there is evidence for the change of the dissociation constant as a function of the degree of titration [5-9]. These changes were assigned to the alteration of the surface charge of the polyion during neutralization. For a quantitative description of this observation, authors either used the modified HENDERSON-HASSELBACH equation or extrapolated the values to zero surface charge [10].

When SZABADKA used Eq. (3) for the calculation of the protonation constants of ethylenediaminetriacetic acid [2] and iminodiacetic acid [3], he found that the protonation constants obtained were independent of the degree of titration in the particular range where the respective constants have their chemical significance.

In the case of ED-resin, however, the constants are so close to each other that Eq. (3) cannot be used for the calculation at the individual steps. Therefore, the independence of a constant of the degree of titration cannot be proved in the above mentioned way. The independence of the constants, however, can be checked in the following way. Once K'_1 and K'_2 have been obtained by Eq. (10) the \overline{pH} can be calculated to a given value of $\overline{\alpha}^*$. These \overline{pH}_{calc} values were compared with those values which were calculated from the experimental data by Eq. (8). This comparison is shown in Fig. 5, where the $\overline{pH}-\overline{pH}_{calc} = \Delta$ values are plotted against $\overline{\alpha}^*$.

In the $0 < \overline{\alpha}^* < 1$ range, where K'_2 has chemical significance, the deviations are really small and are randomly scattered.

In the $1 < \overline{\alpha}^* < 2$ range, however, the empty circles seem to indicate a trend that might be assigned to the fact that the chemically bound chloride content determined in that range is not strictly proportional to the added amount of potassium hydroxide, as was pointed out in the interpretation of



Fig. 5. Dependence of the $\overline{pH} - \overline{pH_{calc}} = \Delta$ on the degree of titration (for details see text)

Fig. 1. If, however, the amount of protons in the resin is calculated directly from the capacity and from the amount of added potassium hydroxide, then slightly different pH values can be obtained. Using these values to calculate the above mentioned Δ parameter, the trend seems to disappear as the full circles of the diagram indicate.

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POTENTIAL OF MEAN FORCE BETWEEN IONS IN ELECTROLYTE SOLUTIONS

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After a brief critical survey of the literature on the different assumptions for the potential of average force, an attempt is made to approximate the "effective pair potential" with respect to the non-linear dielectric behaviour of the solvent without any external fitting procedure. With the decrease of the interionic distance there are lines of forces from one ion to the other going through layers of solvent with different relative permittivity. This monotonously changing relative permittivity is substituted by its volume average, which is a continuous function of the interionic distance. Ionic radii are implied as integration limits. The results obtained are in good agreement with the best approximations in the literature.

1. Introduction

Theoretical calculation of the thermodynamic properties of electrolyte solutions is usually performed in the following way:

a) a potential is assumed for the *pair* interaction of charged ions,

b) it is assumed that these potentials are pairwise additive, *i.e.* they are not affected by the presence of other ions,

c) using some statistical method, the pair-correlation functions, which determine the charge distribution around the ions, are calculated, then

d) from the pair correlation functions and interaction potentials the thermodynamic properties are determined.

From the point of view of concrete applications, the success of the whole procedure depends on the fact whether the assumptions of the pair potentials are realistic enough and whether the statistical mechanical calculations can be carried out accurately with the given pair potentials. Similarly to other theoretical problems, the more realistic the model of pair potentials, the greater the difficulties in the calculations.

In the molecular theory of electrolytes, thermodynamic properties ought to be calculated as the average of all possible configurations of the particles of the solute and solvent molecules. Instead of this complicated procedure, there is a possibility to separate the average behaviour of the

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solvent from that of the solute, if the pair potentials acting between the ions of the solute are substituted by such an "effective" pair potential which is calculated with respect to the *average* behaviour of the solvent. This "effective" pair potential is called *the potential of average force*. What we know about it with all certainty is that at large interionic distances it tends asymptotically to the Coulomb potential (see e.g. refs [1, 2]):

$$\lim_{r_{U^{\rightarrow}}\infty} u_{ij} = z_i z_j e^2 / \varepsilon_0 r_{ij}$$
⁽¹⁾

where u_{ij} is the potential of average force between the *i*th and *j*th type of ions (it may also be that i = j), *e* the elementary charge, the *z*'s are the number of corresponding charges which include their sign too, ε_0 is the relative permittivity of the pure solvent, and r_{ij} the distance between the *i*th and *j*th ion.

Deviations of the pair potentials from the Coulomb law at smaller distances are due to several reasons. On the one hand, the molecular granularity of the solvent can favour certain r_{ij} values and disfavour others, and, on the other hand, the number of solvent molecules in the high electric field of the two ions, which are under conditions different from that of the pure solvent, is higher at small interionic distances compared to the case of large separation distances. On the basis of qualitative considerations, these effects can be unified into a single short-range potential additive to the Coulomb potential which is repulsive independently of the sign of the charges of ions:

$$u_{ij} = u_{ij}^* + z_i z_j e^2 / \varepsilon_0 r_{ij}$$
⁽²⁾

where u_{ij}^* is the short-range term.

The various electrolyte theories differ, among others, in the choice of the model they apply for the calculation of these short-range interactions. After a survey of the most important results obtained so far on the pair potentials, in the present paper we discuss a novel approach to the estimation of u_{ij}^* based on the non-linear dielectric behaviour of the solvent.

2. Literature Survey

The simplest approximation of the repulsive short-range interactions is the so-called "hard core repulsion".

$$u_{ij}^{*} = \begin{cases} 0, & \text{if } r_{ij} \ge a_{ij} \\ \infty, & \text{if } r_{ij} < a_{ij} \end{cases}$$
(3)

where a_{ij} is the smallest possible distance of approach of the *i*-th and *j*-th kind of ions. The models assuming this kind of pair potentials are called *primi*tive models. If, in order to facilitate the statistical mechanical problem, we introduce the simplification that $a_{ij} = a$ for all *i*'s and *j*'s, we obtain the "restricted primitive model".

These kinds of pair potentials are simple enough to handle a as a fitting parameter so that thermodynamic parameters can be written in analytical form with not too rough statistical mechanical approximations. The advantage of these theoretical calculations is that the main features of the electrolytes can be well interpreted by them, but they give numerically correct results only in the case of very dilute solutions.

If one is satisfied with approaching the u_{ij}^* function, which is in reality a continuous function of r_{ij} , with a discontinuous function similar to the primitive model, a more adequate approach of the problem can be obtained applying the hard core repulsion only to the a_{ij} values calculated from the sum of the actual crystallographic radii of ions, and the short-range repulsive (or eventually attractive) interactions resulting from the ion-solvent interaction are described with a "step-function":

$$u_{ij}^{*} = \begin{cases} 0, & \text{if} \quad r_{ij} \ge a_{ij} + a_{s}^{d} \\ b_{ij}, & \text{if} \quad a_{ij} \le r_{ij} < a_{ij} + a_{s} \\ \infty, & \text{if} \quad r_{ii} < a_{ij} \end{cases}$$
(4)

where a_s is the diameter of the solvent molecule, and the b_{ij} values can take over the role of the fitting parameter. If every $b_{ij} = b$ we obtain the restricted version of this model [3]. This kind of pair potential is shown in Fig. 1. Applying this method, thermodynamic parameters cannot be expressed in explicit analytical form, but the numerical methods to be applied need a relatively lesser amount of calculation.

The models which are in better agreement with reality as the above mentioned one try to approach the $u_{ij}^*(r_{ij})$ function in a continuous form. Considering still a very simplified model, LEVINE and WRIGLEY [4] tried to take into account the effect of the polarizability of water molecules in the solvent sphere on the pair potential. They assumed that the ions with +e or -e charges and the solvent molecules are of the same size and their radius is a/3; ions are surrounded inside the sphere of radius a by the solvate shell and the mean polarizability of the complex ion thus formed is α , while the solvent molecules farther off from this distance comprise a continuum with relative permittivity ε_0 . The short-range interaction proves to be always repulsive:

$$u_{ij}^{*} = \frac{e^{2}}{\varepsilon_{0} r_{ij}} \left(b_{3} t^{3} + b_{5} t^{5} + b_{6} t^{6} + \ldots \right)$$
(5)

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Fig. 1. Pair potentials for water as solvent at 298 K according to the primitive model modified with a step function

where $t = a/r_{ij}$ and

$$b_3 = \frac{1}{2D} \left[\left(1 - \frac{1}{\varepsilon_0} \right) \left(1 \pm \frac{2}{3} t^3 \right) (1 + 2v) + Hv \right]$$

$$\tag{6}$$

$$b_5 = \frac{2}{3F} \left(1 - \frac{1}{\varepsilon_0} \right) + \frac{200}{81F^2 \varepsilon_0 a_3} \left(a_s + \frac{8\mu_s}{9e} a^2 \right)$$
(7)

$$b_{6} = \mp \frac{1}{3D} \left[\left(1 - \frac{1}{\varepsilon_{0}} \right) \left(1 + 5v - \frac{3vC}{2D} \right) - \frac{27v^{2}}{2D\varepsilon_{0}} \right] \pm \\ \pm \frac{2560\mu_{s}}{2187D^{2}F\varepsilon_{0}e^{2}a} \left(1 - \frac{1}{\varepsilon_{0}} \right) \left(\frac{3}{2} + \frac{C}{2} + D - \frac{3D\varepsilon_{0}}{\varepsilon_{0} - 1} + \frac{Hv}{2} \right)$$
(8)

where $v = \alpha/a^3$, α_s is the polarizability of the solvent, μ_s is its dipole moment, and

$$C = 1 - v - \frac{1 + 2v}{\varepsilon_0} \tag{9}$$

$$D = 1 - v + \frac{1 + 2v}{2\varepsilon_0} \mp Ct^3 \tag{10}$$

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$$F = 1 + \frac{2}{3\varepsilon_0} \mp 4 t^5 \left(1 - \frac{1}{\varepsilon_0} \right)$$
(11)

and

$$H = \frac{C}{D} \left(1 - \frac{1}{\varepsilon_0} \right) - 4 \left(1 + \frac{1}{2\varepsilon_0} \right) + \frac{9}{2D\varepsilon_0}$$
(12)

The upper one of the double signs in these equations refers to the case of like charged ions, while the lower to that of oppositely charged ones.

In order to describe the repulsive term of the pair potential, Eq. (5) is valid only if r_{ii} is greater than the interionic distance of the two ions together with their solvate spheres, *i.e.* if $t \leq 1/2$. Equation (5) approximates the repulsive effect between dielectric spheres or cavities filled with a continuum of lower relative permittivity. According to electrostatics, these spheres always repel one another and the magnitude of the repulsive forces depends on the ratio of the relative permittivity of the two continua. The model under discussion is more complicated than this: every sphere with lower relative permittivity is divided into two parts, an even smaller sphere characterized by the polarizability of the ion and an outer spherical shell filled with the dielectrically saturated solvent. In spite of these differences, this kind of approximation of the repulsive term of the pair potential is called the cavity model, and the term in the whole pair potential originating from this effect is called the cavity term. (We note that in the theory of ionic solvation one can also use this kind of calculations when operating with spherical shells. These, in spite of their simplicity, give results in good agreement with experimental data [5].)

The above equations in the case of K^+ and F^- ions lead to the curves labelled LW in Fig. 2. It can be seen that the pair potential acting between ions of opposite sign can be approximated satisfactorily with the LEVINE — WRIGLEY equations at distances greater than 0.82 nm, but their continuation marked with dotted line gives still reasonable results even at those distances where the cavity term is meaningless because the solvent spheres merge into each other. On the contrary, the potential acting between like charged ions gives great — and most probably false — oscillations at distances shorter than 0.55 nm.

BAHE [6] applied a physical model which in a certain sense is more realistic than that of the LEVINE—WRIGLEY approximation. BAHE supposed that, in the spherical shell representing the solvate sphere, instead of a medium with constant low permittivity, there is a linear increase of the relative permittivity from a value of n^2 at the surface of the ion, up to the value ε_0 corresponding to the pure solvent. At the same time BAHE made more mathematical simplifications in his calculations, which make his results less precise than those of LEVINE and WRIGLEY.

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Fig. 2. Comparison of pair potentials for water as solvent at 298^{*}K obtained by different approximations (LW – LEVINE and WRIGLEY; B – modified BAHE-equation; C – COULOMB-law)

BAHE starts from the so-called ponderomotoric force:

$$\mathbf{F}_{\mathbf{v}} = \varrho \, \mathbf{E} - \frac{1}{8\pi} \, E^2 \, \nabla \varepsilon + \frac{1}{8\pi} \, \nabla \left(E^2 \frac{\mathrm{d}\varepsilon}{\mathrm{d} \, \ln d} \right) \tag{13}$$

where $\mathbf{F}_{\mathbf{v}}$ is the force acting on a unit volume, ϱ the charge density, \mathbf{E} the electric field, $\nabla \varepsilon$ the gradient of the relative permittivity, and d the mass density of the solvent. BAHE's first approximate assumption is fundamentally false: he neglects the third term of Eq. (13) with the reasoning that, if the medium is incompressible, this term becomes zero.

In order to show that this is erroneous, we transform the third term of Eq. (13) as follows:

$$E^{2} \frac{\mathrm{d}\varepsilon}{\mathrm{d}\ln d} = \mathbf{D} \mathbf{E} \frac{\mathrm{d}\ln\varepsilon}{\mathrm{d}\ln d}$$
(14)

where **D** is the dielectric displacement. It is obvious that the $d \ln e/d \ln d$ factor expresses the dependence of the relative permittivity, *i.e.* the dipole density, of the solvent on the mass density. This quantity is unity in case of

polar liquids with regular electric equation of state. (In this case the dipole density is proportional to the mass density, because the number of dipoles in unit volume can be increased only by increasing proportionally the number of molecules in the system.) When considering liquids with anomalous electric equation of state, this quantity can differ from unity, but it may never become zero, since this would mean that the number of molecules per unit volume can be increased without increasing the number of dipoles. This is impossible in case of polar molecules. So the differential quotient in question has nothing to do with compressibility.

Fortunately, this error of BAHE can be corrected rather easily. We should assume only that $d \ln \varepsilon/d \ln d \approx d \ln \varepsilon_0/d \ln d$ which is equivalent to the assumption that the structure of the medium (and also its KIRKWOOD-factor) does not change too much on compression. This holds by all means in the case of normal liquids but for anomalous ones it is valid only as an acceptable approximation. For instance, for pure water at room temperature [8]. $d \ln \varepsilon_0/d \ln d = 0.707$, *i.e.* the error of the above approximation would be 30% in that part of the space around the ions where the structure of water is completely destroyed as a result of the high-field effect.

Applying this approach and following BAHE's integration procedure [6] we obtain for the repulsion potential:

$$u_{ij}^{*} = \frac{z_{i}^{2} z_{j}^{2} e^{2}}{\varepsilon_{0}} \left[\frac{V_{s}}{16\pi} \cdot \frac{\Delta \varepsilon}{b} \left(1 + \frac{\mathrm{d} \ln \varepsilon_{0}}{\mathrm{d} \ln d} \right) \frac{1}{\varepsilon_{0} r_{ij}^{3}} + \frac{3V_{s}}{128\pi} \cdot \frac{\mathrm{d} \ln \varepsilon_{0}}{\mathrm{d} \ln d} \frac{1}{r_{ij}^{4}} \right]$$
(15)

where V_s is the volume of the solvent layer of a thickness b around the ion and $\Delta \varepsilon$ is the change of relative permittivity within this layer.

Equation (15) transforms into the original BAHE equation if we put zero in place of d ln ε_0 /d ln d. If one does not handle the constants of the equation as fitting parameters, as BAHE did, then for KF we obtain curve B of Fig. 2.

All of these models take into account only one feature of the interaction of the solvate spheres, the so-called "cavity-interaction". Using the idea of GURNEY [9], RAMANATHAN and FRIEDMAN [10] took into account the work needed to remove the solvent, expelled from the merging solvate shells, from the field of ions to infinity. This term of the repulsion potential is the so-called GURNEY term:

$$u_{ij,0}^* = A_{ij} \frac{V_{\rm m}}{V_{\rm s}} \tag{16}$$

where $V_{\rm m}$ is the mutual volume (the volume of the common part of the solvate shells) calculated for one mol of ion pairs in a distance r_{ij} , while now $V_{\rm s}$ is the molar volume of the solvent under normal conditions. A_{ii} is a fitting param-

eter to be chosen so that the thermodynamic and other macroscopic parameters (e.g. electric conductivity) calculated with the given potential agree best with experimental ones.

For the mutual volume, the authors give the following estimation:

$$V_{\rm m} = \begin{cases} \pi \left[-\frac{(r_i^2 - r_j^2)^2}{4r_{ij}} + \frac{2}{3}(r_i^3 + r_j^3) - \frac{1}{2}r_{ij}(r_i^2 + r_j^2) + \frac{1}{12}r_{ij}^3 \right], \\ \text{if} \quad r_{ij} \le r_i + r_j + 2r_s \\ 0, \quad \text{otherwise} \end{cases}$$
(17)

where r_i and r_j are the PAULING radii of ions, and r_s^s is the radius of the solvent molecule.

RAMANATHAN and FRIEDMAN took into consideration the cavity interaction only with the term of the LEVINE-WRIGLEY potential, which depends linearly on r_{ij}^{-4} . They also introduced the "core-potential", the interaction of the bare ions, which is repulsive, too :

$$u_{ij,c}^* = \frac{Me^2}{9N(r_i + r_j)} \left(\frac{r_i + r_j}{r_{ij}}\right)^9 \tag{18}$$

where M is the MADELUNG constant of the appropriate crystal of the electrolyte solute and N is the coordination number of the ions in this crystal. Thus the whole repulsive potential is:

$$u_{ij}^{*} = u_{ij,c}^{*} + u_{ij,G}^{*} + \frac{\varepsilon_{0} - \varepsilon_{c}}{2\varepsilon_{0} + \varepsilon_{c}} (z_{i}^{2} r_{j}^{3} + z_{j}^{2} r_{i}^{3}) \frac{e^{2}}{2\varepsilon_{0} r_{ij}^{4}}$$
(19)

where ε_c is the mean relative permittivity of the cavity appropriate to the solvated ion. The cavity term in Eq. (19) gives distinctly smaller repulsion than the LW-potential. This deficiency can be partly compensated for by the A_{ii} parameter which is left to be fitted.

Figure 3 shows that the curve obtained by RAMANATHAN and FRIEDMAN in the case of KF is not the same as the LW-potential. One reason of this difference can be the fact that out of the three different A_{ij} parameters (A_{KF}, A_{KK}, A_{FF}) they fitted in fact only one to experimental thermodynamic values, so they obtained a "consistent" but not certainly real pair potential.

None of these models considered the molecular granularity of the solvent, for they took it into account as a continuum. One of the very simplified effect of "granularity" can be that it adds to the above calculated interactions, partly with repulsion potential (when the solvent molecules can be arranged within the r_{ij} distance only if they are pressed together a little) and partly with attractive potential (when the molecules of the solvent can fill up the space within the interionic distance only when pulled apart). As a result,

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Fig. 3. Pair potentials for K^+ and F^- in water as solvent at 298 K according to RAMANATHAN and FRIEDMAN (solid line). 1 — repulsion of ion cores; 2 — cavity interaction; 3 — GURNEY term. The COULOMB potential is represented with dotted line

the effect of granularity produces "waves" on the originally smooth pair potential, as can be seen in Fig. 4. Here the additive "waves" are taken from the approximate MONTE-CARLO studies on pure water [11].



Fig. 4. Modified pair potential for water as solvent at 298 K in the case of the primitive model taking into account the granularity of the solvent

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Although the assumption of additivity is usually a good approximation, in reality MONTE-CARLO calculations would be needed, which take into account as exactly as possible both the interactions of ions and solvent molecules and that of the solvent molecules with each other and which neglect neither the effect of hydrogen bonds nor the mutual polarizability. Unfortunately, this kind of procedure requires so much computer time that it cannot be carried out yet. A computation made so far (which considers the ions and solvent molecules as non-polarizable rigid spheres and constructs the potential



Fig. 5. Pair potential calculated for 298 K by the MONTE-CARLO method considering the ion-dipole and dipole-dipole interaction. The COULOMB potential represented for comparison was calculated with $\varepsilon_0 = 7.8$

^from the ion-dipole and dipole-dipole interactions) did not reveal basically new results compared to those with the assumption of additivity, even though it took 80 hours on an IBM 7094 computer [12] (Fig. 5).

The steep descending region of the curve at small interionic distances is probably unreal and is due to the fact that the model is approximate. In the case of polarizable solvent molecules, a larger work than that calculated is required to partially remove the innermost solvate sphere from between the two ions approaching each other successively to a distance of contact.

From the results of the literature reviewed above, it can be concluded that our knowledge on the potential of mean force between ions is still unsatisfactory. One aim of further studies may be the derivation of equations which can be applied with relative ease in the statistical mechanical theory of electrolytes, but the simplicity would not be attained by *a priori* undetermined fitting parameters, since with such pair potentials the theory would not be predictive. In the following section of this paper we attempt to derive a pair potential with no fitting parameters.

3. Approximation of the potential of mean force with respect to the non-linear dielectric behaviour of the solvent

Let us restrict ourselves to the case of ions with equal absolute value of charges $\pm z$. Suppose that ions are embedded in a continuous dielectric whose relative permittivity depends on the electric field strength as a continuous function of the space coordinates. In this case, along the surfaces where the relative permittivity changes infinitesimally, there are infinitesimal uncompensated polarization charges in the dielectric, and there one part of the lines of forces coming from the ions terminate (cf. Fig. 6, where as an example, we sketched the case of oppositely charged ions). Ions are surrounded by a layer of low relative permittivity and here the density of the lines of forces is the greatest, in the following layer, with higher relative permittivity there



Fig. 6. Representation of the interaction of two oppositely charged ions with a field-dependent relative permittivity. Solid lines are the lines of forces of the field, the regions with different relative permittivities are separated by dotted lines

are fewer lines of force, etc. Finally one arrives at such a large distance from the ion where the relative permittivity of the pure solvent predominates. There the density of the lines of forces corresponds to a relative permittivity ε_0 . If ions are as far away from each other that the regions of their environments with lower relative permittivity do not merge, then the potential of mean force will be the COULOMB law with ε_0 in the denominator.

However, if the regions of lower relative permittivity merge, and this is the case when the interionic distance is shortened, some lines of forces can reach from one ion to the other through a medium of relative permittivity



Fig. 7. To the approximate derivation of pair potential (see text)

^vower than ε_0 . For ions close to each other this region of the space is expanded. due to the effect of the common field, more than for ions far from each other, With the decrease of the interionic distance more and more lines of force reach the other ion through regions with successively lower permittivity.

The polarization of the solvent layers with lower relative permittivity in the common field of the two ions and the effect of this polarization on the change of the forces acting between these ions would be a difficult task to calculate. Let us simplify the model as follows: suppose that the outer hemisphere of both ions does not change when the distance between the two ions decreases, *i.e.* assume that a significant mutual polarization exists only in the space between the two ions. Let the average relative permittivity of the region, seen from both ions under a solid angle $\pi/2$ (Fig. 7), be a function of the field. On the basis of the arguments described in our previous paper [13], let us replace the relative permittivity changing from point to point with its *volume average* within this space. If the distance decreases, ε would be considerably lower than ε_0 .

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In order to make a simple averaging procedure, the volume in question is approximated with an octahedron whose two opposite vertices are at the center of the two ions. We have shown [13] that in this region of the space the average relative permittivity is with good approximation:

$$\varepsilon = \varepsilon_0 (1 - g e^{-h f_{\rm a} r}) \tag{20}$$

where g and h are constants (for water at 25 °C their values is 12.0 and 1.27×10^8 cm⁻¹, respectively), $r = r_{ij}$, and

$$f_{\rm a,+-}^2 = \frac{2/9 - 0.6891(a_{\rm a}^3 + a_{\rm c}^3)/r^3}{z[2.0019 - 2.2214(a_{\rm a} + a_{\rm c})/r]}$$
(21)

where a_a and a_c are the crystallographic radii of the anion and cation, respectively, which appear as integration limits in the derivation of this formula.

The relative permittivity of a similar region between like charged ions can be calculated with Eq.(20) but in this case one must take into account that in the middle of the distance between the two ions the orientation effect of the electric field cancels. Thus it is obvious that in region 2 in the Appendix of ref. [13] the component of the vector of dielectric displacement lying in the direction of the straight line going from one ion to the other is zero.

Applying the approximation of ref. [13] in any other aspect we obtain:

$$f_{a,++}^2 = \frac{2/9 - 1.3782a_c^3/r^3}{z(1.980 - 4.4428a_c/r)}$$
(22)

 f_a^2 , - can be calculated analogously, but a_a should be written instead of a_c . With this approximation the volume of the region between the ions

with relative permittivity different of that of pure solvent is:

$$V = r^3/6 \tag{23}$$

If ions are far apart from each other, a portion of 1/6 of the lines of forces cross this region of the space, since viewing it from the center of one of the ions, this region is seen under one sixth of the total solid angle. Let us suppose that at finite interionic distances the partition of the Coulomb interaction acting on the dielectric, which can be characterized with ε_0 and ε , is the same:

$$u_{ij,\text{ COUL.}} = \pm \frac{5(ze)^2}{6\varepsilon_0 r} \mp \frac{1}{6} \int_{r}^{\infty} \frac{(ze)^2}{\varepsilon r'^2} \,\mathrm{d}r'$$
(24)

where, of the double signs, the upper one always refers to the case of like and the lower to that of oppositely charged ions. Inserting Eq. (20) and integrating with the neglect of the terms of higher order than r^{-2} , we have:

$$u_{ij, \text{ COUL}} = \pm \frac{(ze)^2}{\varepsilon_0} \left[\frac{1}{r} + \frac{1}{6hf_{a,ij}} \left(\ln \frac{\varepsilon_0}{\varepsilon} \right) \frac{1}{r^2} \right]$$
(25)

It is obvious that the COULOMB potential in the case under discussion is greater in its absolute value than in the case corresponding to a relative permittivity ε_0 and with the increase of r it tends rapidly to the simple COULOMB law, because ε tends to ε_0 exponentially with r.

Yet the field of the two ions attracts also the solvent molecules of the space between them. In order to decrease the interionic distance, we have to transfer the solvent characterized by ε into the region outside the ions, which is characterized by ε_0 . This always requires an input of work, thus it increases the repulsion between ions. Let us denote this work by u_s and divide it into two components u_{s1} and u_{s2} . The term u_{s1} is the work needed when the region between the ions is decreased to a volume corresponding to r starting from the state where the ions are at infinite distance, whereas the solvent in question is removed from the system and is transferred into a state of the pure solvent. The u_{s2} term is the work required when this free solvent is transferred into the region of the solution characterized with ε_0 . Since when $r \to \infty$, u_s must be zero, we write:

$$u_{s2} = \lim_{r \to \infty} u_{s1} \tag{26}$$

 u_{s_1} can be calculated as follows:

$$u_{s_1} = -\int_{V}^{\infty} g_{V_1} \, dV' = -\frac{1}{2} \int_{r}^{\infty} r'^2 g_{V_1} \, dr'$$
(27)

where g_{V1} is the free enthalpy density of the interionic region:

$$g_{V1} = -\int_{r'}^{\infty} F_{V1} \, \mathrm{d}r'' \tag{28}$$

Here \mathbf{F}_{V1} is the volume force defined in eq. (13).

When calculating the average behaviour of the region in between the ions [13], we used the assumption that the relative permittivity of this region is the same as that of the spherical layer at a distance $x'' = f_a r''$ from a single point charge. Thus $\nabla \varepsilon$ can be replaced by the average gradient

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$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}x''} = \frac{1}{f_{\mathrm{a},ij}} \frac{\mathrm{d}\varepsilon}{\mathrm{d}r''} \tag{29}$$

Thus the ponderomotoric force (considering also that there are no free charges in the region investigated) becomes:

$$F_{V1} = -\frac{1}{8\pi} \cdot \frac{(ze)^2}{\varepsilon^2 x''^4} \frac{\mathrm{d}\varepsilon}{\mathrm{d}x} + \frac{1}{8\pi} \frac{d}{\mathrm{d}x} \left[\frac{(ze)^2}{\varepsilon x''^4} \frac{\mathrm{d}\ln\varepsilon}{\mathrm{d}\ln d} \right]$$
(30)

Simplifying this with the assumption:

$$s = \frac{\mathrm{d}\,\ln\varepsilon}{\mathrm{d}\,\ln d} \simeq \frac{\mathrm{d}\,\ln\varepsilon_0}{\mathrm{d}\,\ln d} \neq f(x'') \tag{31}$$

we have:

$$F_{V1} = \frac{(ze)^2}{8\pi} \left[(1+s) \frac{1}{x''^4} \cdot \frac{d}{\mathrm{d}x''} \left(\frac{1}{\varepsilon} \right) - \frac{4s}{\varepsilon x''^5} \right]$$
(32)

Substituting this into Eq. (28) and neglecting again the higher order terms, we obtain:

$$g_{V1} = -\frac{(ze)^2}{8\pi\varepsilon_0} \left(\frac{1}{x^{\prime 4}} + \frac{4}{hx^{\prime 5}} \ln \frac{\varepsilon_0}{\varepsilon} \right) + \frac{(1+s)(ze)^2}{8\pi\varepsilon x^{\prime 4}}$$
(33)

In order to obtain an expression of g_{V1} that can be approximately integrated analytically, we expand the logarithmic term into series and estimate g_{V1} as follows:

$$g_{V1} = -\frac{(ze)^2}{8\pi\varepsilon_0} \left[\frac{1}{x^{\prime 4}} - \frac{4}{hx^{\prime 5}} \left(1 - \frac{\varepsilon}{\varepsilon_0} \right) \right] + \frac{(1+s)(ze)^2}{8\pi\varepsilon x^{\prime 4}}$$
(34)

Inserting this into Eq. (27) and integrating, we obtain:

$$u_{s1} = \frac{(ze)^2}{16\pi f_{a,ij}^4 \varepsilon_0} \left[\left(\frac{1+s}{f_{a,ij}hr^2} + \frac{4}{f_{a,ij}^2 h^2 r^3} \right) \left(\ln \frac{\varepsilon_0}{\varepsilon} \right) - \frac{s}{r} \right]$$
(35)

The limit of this when $r \to \infty$ is:

$$u_{s2} = \frac{s(ze)^2}{16\pi f_{a,ij}^4 \varepsilon_0 r}$$
(36)

Thus the total pair potential (indicating again the indices ij referring to the kinds of ions) is:

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$$u_{ij} = u_{ij,c}^* \pm \frac{(ze)^2}{\varepsilon_0} \left[\frac{1}{r_{ij}} + \frac{1}{6hf_{a,ij}} \left(\ln \frac{\varepsilon_0}{\varepsilon} \right) \frac{1}{r_{ij}^2} \right] + \frac{(ze)^2}{16\pi f_{a,ij}^4 \varepsilon_0} \left(\frac{1+s}{f_{a,ij}hr_{ij}^2} + \frac{4}{f_{a,ij}^2 h^2 r_{ij}^3} \right) \left(\ln \frac{\varepsilon_0}{\varepsilon} \right)$$
(37)

where $u_{ij,c}^*$ is the core term given in Eq. (18). It is obvious that our approximation differs at some points from those mentioned in Section 2. On one hand we



Fig. 8. Pair potentials for K^+ and F^- in water as solvent at 298 K (for comparison: LW - LEVINE and WRIGLEY; C - COULOMB potentials)

took into account that the COLUOMB interaction increases because of the decrease of the relative permittivity of the medium [cf. the second part of the second term of Eq. (37)]. On the other hand, the radius of bare ions appears explicitly in the equation (through the f_a values), thus there is no need for a fitting procedure like that applied in ref. [10].

In its physical meaning the above derivation also considers effects like the "cavity-interaction" and "GURNEY-term", since from both terms in the expression of the ponderomotoric force there originates a term depending on the dielectric gradient, which is ultimately nothing else than the "cavity interaction" of an abundance of infinitely thin concentric spherical layers with successively lower relative permittivity.

The rest of the terms of the volume force $\mathbf{F}_{\mathbf{v}}$ can be connected with the GURNEY term, but in our procedure it does not have to be approximated with a discontinuous function. The analogy is clear if we consider the factor $(1 - 1/\varepsilon_0)$ from the LW potential which can be found in the higher order terms of Eq. (37), as the approximation of the first two terms of power series of $\ln (\varepsilon_0/\varepsilon)$. It should also be noted that the dependence of the repulsive terms on r_{ij} is but seemingly of lower order than those in earlier approximations, because the fast decrease of the term $\ln (\varepsilon_0/\varepsilon)$ with the increase of r_{ij} implies in fact a higher order dependence.



Fig. 9. Pair potentials for alkali chlorides in water as solvent at 298 K (for comparison: C - COULOMB potentials)

In Fig. 8 it can be seen that the LW potential and the potential calculated in the present work (labelled with RG) practically coincide. The difference is mainly due to "core-repulsion" which is not included in the LW potential.

From Fig. 9 it can be concluded that the smaller ions result in a greater repulsive effect which is in accordance with their greater tendency for solvation. Thus the pair potentials obtained in the present work seem rather realistic in spite of the approximations involved.

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KINETICS OF THE Co₂(CO)₈-DEPENDENT REACTIONS OF HCo(CO)₄ WITH OLEFINS

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Carbonylation and hydrogenation with $HCo(CO)_4$ of isolated or with electronwithdrawing group conjugated carbon-carbon double bonds generally require the presence of $Co_2(CO)_8$. Both reactions are of half order for $Co_2(CO)_8$ and of first order for the olefin. The ratio of rates of carbonylation and hydrogenation depends on the ratio of the CO and $HCo(CO)_4$ concentrations and decrease in the order: heptene-1 > > heptene-2 or -3 > ethyl acrylate. Higher temperature favours hydrogenation over carbonylation. Using $DCo(CO)_4$, there is practically no kinetic isotope effect in carbonylation, but a medium effect was observed in hydrogenation.

Introduction

The reaction between $HCo(CO)_4$ and an olefin is regarded as a component of the hydroformylation catalytic cycle. The main products of this stoichiometric reaction are aldehydes (at low olefin/ $HCo(CO)_4$ ratios) or acylcobalt tetracarbonyls (at high olefin/ $HCo(CO)_4$ ratios in the presence of CO). Saturated hydrocarbons are formed as by-products [1]. In the widely accepted mechanism of the reaction, alkylcobalt and acylcobalt carbonyls are assumed as intermediates [2].

 $\begin{aligned} \mathrm{RCH} = \mathrm{CH}_2 + \mathrm{HCo}(\mathrm{CO})_4 &\longrightarrow \mathrm{RC}_2\mathrm{H}_4\mathrm{Co}(\mathrm{CO})_4 \\ \xrightarrow{+\mathrm{CO}} & \mathrm{RC}_2\mathrm{H}_4\mathrm{COCo}(\mathrm{CO})_4 \xrightarrow{\mathrm{HCo}(\mathrm{CO})_4} \mathrm{RC}_2\mathrm{H}_4\mathrm{CHO} + \mathrm{Co}_2(\mathrm{CO})_8 \\ \\ \mathrm{RC}_2\mathrm{H}_4\mathrm{Co}(\mathrm{CO})_4 \xrightarrow{+\mathrm{HCo}(\mathrm{CO})_4} \mathrm{RC}_2\mathrm{H}_5 + \mathrm{Co}_2(\mathrm{CO})_8 \end{aligned}$

Kinetic information about the above reactions is scarce. From the CO absorption curves, TAKEGAMI and co-workers derived the following order of reactivity: *n*-butyl vinyl ether, $10^3 >$ styrene, 20 > ethyl acrylate, 5 > pentene-1 [3]. Later it was found that the kinetics of CO uptake in the reaction of ethyl vinyl ether and phosphine-substituted cobalt carbonyl hydride showed a first order dependence of the olefin and the hydride concentrations and the addition of phosphine retarded the reaction [4]. To our knowledge, no other detailed kinetic study of acylcobalt tetracarbonyl formation has been made till now. There is some additional information available on the stoichiometric

hydrogenation of diethyl fumarate by $HCo(CO)_4$, where we have found that CO decreases and $Co_2(CO)_8$ increases the rate [5]. A completely different kinetic behaviour was found for olefins in which the carbon-carbon double bonds is in conjugation with phenyl ring(s) [6]. In those cases neither CO nor $Co_2(CO)_8$ exerts any influence on the rate of hydrogenation.

Experimental

The olefins and solvents were distilled under carbon monoxide. Pale yellow coloured 0.6 M stock solution of $HCo(CO)_4$ and 0.24 M stock solution of $Co_2(CO)_8$ were prepared in *n*-octane. $DCo(CO)_4$ was prepared from $HCo(CO)_4$ solutions by exchange with D_2O . The concentrations of the $HCo(CO)_4$ and $DCo(CO)_4$ solutions were determined by alkaline titration. Kinetic runs were performed under CO in a gasometric apparatus using an appropriate

Kinetic runs were performed under CO in a gasometric apparatus using an appropriate large buffer flask connected to the levelling vessel of the gas burette. Experiments were run between 47.8 and 290.4 kPa total pressures. The reaction was started by injecting the olefin into the vigorously stirred and thermostated solutions of $HCo(CO)_4$ and $Co_2(CO)_8$. The initial rate of CO uptake was calculated from the change of gas volume as a function of time. The initial rate of hydrogenation was calculated from the amount of saturated compounds formed during a few per cent $HCo(CO)_4$ conversion after start. The amount of saturated compounds mixtures after quenching with pyridine. (Hewlett-Packard 5830/A, SE 30, 10 m glass capillary column, 40 °C, 2 mL argon/min, FID. In the case of ethyl acrylate: SP 2100, 30 m glass capillary column, 40 °C, 1.5 mL argon/min, FID.)

A foliated reaction vessel was used to run the reaction in darkness.



Fig. 1. CO Absorption vs. time plots for the reaction of heptene-1 with $HCo(CO)_4$ in heptane solution at 15 °C. Initial concentrations: [heptene-1] = 1.02 M, [HCo(CO)₄] = 0.120 M, [CO] = 0.0105 M

Olefin	[Olefin] (M)	$ [\mathrm{HCo(CO)_4}] \cdot 10^2 \\ (M) $	$[Co_2(CO)_8] \cdot 10^2$ (M)	$r_{ m CO} \cdot 10^{6}$ (M s ⁻¹)	$r_{\rm H} \cdot 10^{6} \ (M \ { m s}^{-1})$
heptene-1 ^d	0.313	5.76	<0.2°	< 0.4	0.0
heptene-1	0.157	1.53	4.8	1.40	0.092
heptene-1	0.157	2.90	4.8	2.25	0.28
heptene-1	0.157	8.12	4.8	4.0	1.2
allylbenzene	0.139	2.09	$< 0.2^{\circ}$	0.1	0.0
allylbenzene	0.139	2.09	5.65	1.3	0.23
4-Me-pentene-1	0.790	2.92	4.8	10.1	0.10
2-Me-pentene-1	0.811	2.92	4.8	< 0.4	
2-Me-pentene-1	0.811	8.88	12.2	1.03	
heptene-2 ^e	0.690	1.53	4.8	0.64	
heptene-2 ^e	0.690	2.90	4.8	0.95	
heptene-2 ^e	0.690	8.12	4.8	1 14	
trans-heptene-2	0.714	8.88	4.8	0.75	0.5
hentene-2°	0.690	16.94	4.8	1.95	0.5
hentene-3 ^f	0.715	1.54	4.8	1.19	
hentene-3f	0.715	2 00	4.8	1.12	
heptene-3t	0.715	8.12	4.8	3.41	
trans-hentene-3	0.715	9.98	4.8	0.71	0.00
hentene-3t	0.715	16.94	4.8	4.34	0.00
evelohevene	1.07	2 00	4.9	0.9	
evelohexene	1.97	0.19	4.0	0.25	
ethyl corvlete	0.120	0.12	4.0	0.55	
athyl acrylate	0.139	2.09	5.65	19.0	
athyl acrylate	0.139	2.00	16.4	20.9	
athyl arotonata	0.139	2.00	10.4	20.2	
athyl crotonate	0.300	4.1	< 0.2	< 0.1	
athed anotomate	0.300	4.1	4.0	0.07	
ethyl crotonate	0.300	4.1 4.1	17.0	1.03	
1-Cl-propene-1 ^g	0.300	4.1	4.7	1.72	
1-Cl-propene-1g	0.300	4.1	17.1	3.42	
butyl vinyl ether	0.139	2.08	$< 0.2^{\circ}$	3.6	
ethyl vinyl ether	0.139	2.08	$< 0.2^{\circ}$	3.32	
ethyl vinyl ether	0.139	2.08	5.65	4.15	
butyl vinyl ether	0.139	2.08	16.4	5.44	
styrene ^h	0.139	2.07	<0.2°	8.5	4.5
styrene ^h	0.139	2.07	16.4	8.5	4.7
4-Me-styrene	0.139	2.09	$< 0.2^{\circ}$	11.4	12.2
4-Me-styrene	0.139	2.09	5,65	11.0	15
2-Me-styrene	0.141	2.09	$< 0.2^{\circ}$	14.1	10.5
2-Me-styrene	0.139	2.09	5.65	13.5	11.3

The influence of $Co_2(CO_8)$ on the initial rate of CO absorption $(r_{CO})^a$ and hydrogenation $(r_H)^b$ in the reaction of $HCo(CO_4)$ with different types of olefins in octane solution under CO at 15 °C Total pressure: 99.0 \pm 0.5 kPa

Table I

^a r_{CO} in mol CO absorbed/L/s
^b r_H in mol saturated compound formed/L/s
^c Uncertain because the HCo(CO)₄ solution despite careful preparation always contains a small amount of Co₂(CO)₈ which can be estimated from IR absorbance values [8]
^d In heptane solution; ^e mixture of 47% trans and 53% cis; ^t mixture of 30% trans and 70% cis; ^g cis and trans; ^h for more detail cf. [7]

Results and Discussion

Olefins in which the carbon-carbon double bond is isolated (e.g. heptene-1 heptene-2, allylbenzene, etc.) or conjugated with electron-withdrawing group(s) (e.g. ethyl acrylate) generally require the presence of $\text{Co}_2(\text{CO})_8$ for a facile reaction with $\text{HCo}(\text{CO})_4$.

Figure 1 shows the characteristic course of the observed CO absorption in the reaction of heptene-1 with $HCo(CO)_4$. In the absence of initially added $Co_2(CO)_8$ the CO uptake starts very slowly, but accelerates as the colour of the reaction mixture turns from the originally pale yellow, through various

Table II

Initial CO absorption rates (r_{CO}) in the presence of $HCo(CO)_4$ and heptene-1 in heptane solution at various concentrations of initially added $Co_2(CO)_8$ under CO atmosphere at 15 °C Total pressure: 99.3 \pm 0.5 kPa. Stirring rate: 600/min. Initial concentrations of $[HCo(CO)_4] = 0.120 M$, [heptene-1] = 1.02 M

18.1
17.8
18.0
17.8
18.1

^a Stirring rate: 1000/min. ^b Stirring rate: 300/min.

Table III

Initial CO absorption rates $(r_{\rm CO})$ and initial stoichiometric hydrogenation rates $(r_{\rm H})$ in the presence of $HCo(CO)_4$ and octene-1 in heptane solution at various concentrations of initially added $Co_2(CO)_8$ under CO atmosphere at 15 °C

Total pressure: 99.3 \pm 0.5 kPa. Initial concentrations of $[HCo(CO)_4] = 0.083 M$, [octene-1] = = 0.508 M

$\begin{bmatrix} \operatorname{Co}_{\mathfrak{g}}(\operatorname{COO})_{\mathfrak{g}} \end{bmatrix}$ (M)	$r_{\rm CO} \cdot 10^6 \ (M \cdot { m s}^{-1})$	$\frac{r_{\rm CO} \cdot 10^5}{[{\rm Co}_2({\rm CO})_8]^{0.5}}$	$r_{\rm H} \cdot 10^6 \ (M \cdot { m s}^{-1})$	$\frac{r_{\rm H} \cdot 10^{\rm 5}}{[{\rm Co}_2({\rm CO})_8]^{\rm 0.8}}$
0.0190	9.5	6.88	2.0	1.45
0.0476	15.8	7.23	3.3	1.45
0.0476	15.0	7.18	3.3	1.45
0.0476	15.7	7.23	_	
0.1852	17.9	6.94	6.2	1.43
0.1852			5.9	1.36

Table IV

Initial CO absorption rates (r_{CO}) in the presence of $HCo(CO)_4$, $Co_2(CO)_8$ and heptene-1 in heptane solution under CO atmosphere at 15 °C at various concentrations of heptene-1 Initial concentrations of $[HCo(CO)_4] = 0.060 \ M$, $[Co_2(CO)_8] = 0.122 \ M$. Total pressure: $98.8 + 0.4 \ kPa$

[heptene-1] (M)	$r_{\rm CO} \cdot 10^6 \ (M \cdot { m s}^{-1})$	r _{CO} · 10 ⁸ [heptene-1]
0.495	21.2	4.28
0.99	43.7	4.41
0.99 ^a	42.7	4.32
1.98	88.8	4.48
3.13	135.0	4.32

* Experiment in darkness

Table V

Initial CO absorption rates $(r_{\rm CO})$ and initial hydrogenation rates $(r_{\rm H})$ in the presence of $HCo(CO)_4$ and ethyl acrylate in octane solution at various concentrations of initially added $Co_2(CO)_8$ under CO atmosphere at 15 °C

Initial concentrations of $[HCo(CO)_4] = 0.0208 M$, [ethyl acrylate] = 0.139 M. Total pressure: 99.0 kPa

[Co ₂ (CO) ₈] (M)	$r_{\rm CO} \cdot 10^6$ $(M \cdot { m s}^{-1})$	$\frac{r_{\rm CO} \cdot 10^{6}}{[{\rm Co}_2({\rm CO})_8]^{0.5}}$	$r_{\rm H} \cdot 10^5 \ (M \cdot { m s}^{-1})$	r _H · 10 ⁵ [Co ₂ (CO) ₈] ^{0.5}
0.0168	6.53	5.04	4.8	3.70
0.0189	6.83	4.97		
0.0565	12.0	5.07		
0.0960	15.5	5.00	11	3.55
0.164	20.2	4.99		

shades of yellow, to brown. In parallel with this colour change, the infrared spectra of the reaction mixture show the formation of acylcobalt tetracarbonyl and $\text{Co}_2(\text{CO})_8$. Practically the same conversion can be achieved in the presence of initially added $\text{Co}_2(\text{CO})_8$, but the reaction is much faster. The CO uptake starts in this case at a maximum rate.

If the carbon-carbon double bond in the olefin is in conjugation with electronegative groups which are able to exert a positive mesomeric effect (e.g. vinyl alkyl ethers, propenyl chloride, etc.) $\text{Co}_2(\text{CO})_8$ accelerates the CO absorption, but the reaction starts at an appreciable rate without initial addition of $\text{Co}_2(\text{CO})_8$. These olefins will be treated in detail in a separate publication.

The third group of olefins where the carbon-carbon double bond is conjugated to a phenyl ring (e.g. styrene) does not require the presence of $\text{Co}_2(\text{CO})_8$

Table VI

[HCo(CO) ₄] (M)	$[CO]^{a} \cdot 10^{2}$ (M)	$rac{r_{ ext{CO}} \cdot 10^6}{(M \cdot ext{s}^{-1})}$	
0.0204	1.057	15.0	
0.0407	1.040	25.5	
0.0814	1.040	38.7	
0.120	0.479	73.5	
0.120	1.049	47.7	
0.120	1.050	48.5	
0.120	2.21	30.3	
0.120	3.18	26.3	
0.160	1.037	54.5	
0.200	1.032	55.0	

Initial CO absorption rates (r_{CO}) in the presence of $HCo(CO)_4$, $Co_2(CO)_8$ and heptene-1 under CO atmosphere in heptane solution at various total pressures and $HCo(CO)_4$ concentrations at 15 °C Initial concentrations: [heptene-1] = 1.02 M, $[Co_2(CO)_8] = 0.072 M$

^a Calculated using solubility data for heptane [10] and for heptene-1, see Table VII

Table VII

Solubility^a of CO in heptene-1 expressed in Oswald's absorption coefficient (λ)

Temp. (°C)	λ ^b		
15	0.372		
25	0.364		
35	0.355		
45	0.347		
55	0.339		

^a The solubility of CO in heptene-1 at various temperatures was measured by the gas saturating method described in the literature [11]

^b = v/w/p; v = volume of CO in mL at 101.3 kPa at 0 °C;

w = weight of heptene-1 in gramme

p = pressure of CO in kPa/101.3

for the reaction, and the rates are independent of the CO concentration. These results have been published elsewhere [7].

Characteristic examples for all three groups of olefins are compiled in Table I.

[Octene-1] (M)	$\begin{bmatrix} Co_2(CO)_8 \end{bmatrix} \cdot 10^2 \\ (M) \end{bmatrix}$	$ \begin{array}{c} [\mathrm{HCo(CO)}_{t}] \cdot 10^{2} \\ (M) \end{array} $	[CO] · 10 ² (M)	$r_{ m CO} \cdot 10^{6}$ $(M \cdot s^{-1})$	$r_{ m H} \cdot 10^6 \ (M \cdot s^{-1})$
0.1016	4.97	0.950	1.039	0.550	0.044
0.1016	5.00	0.953 ^a	1.040	0.534	0.020
0.1016	5.00	1.190	1.016	0.683	0.067
0.1016	5.00	1.183 ^a	1.016	0.667	0.043
0.1016	5.04	1.50	1.014	0.833	0.137
0.1016	5.00	1.91	1.062	0.950	0.183
0.1016	5.00	1.92 ^a	1.060	0.983	0.111
0.103	4.60	1.93	1.051	0.983	0.217
0.103	4.60	1.92^{a}	1.051	0.933	0.119
0.1016	5.05	2.86	1.061	1.33	0.316
0.1016	5.00	4.56	1.035	1.78	0.678
0.1016	5.00	8.30	1.034	1.92	1.25
0.113	5.55	9.22	1.035	2.58	1.75
0.508	4.76	8,30	0.510	20.6	5.2
0.508	4.76	8.30	1.049	15.0	3.3
0.508	4.76	8.30	2.040	11.8	1.67

Initial CO absorption rates $(r_{\rm CO})$ and initial stoichiometric hydrogenation rates $(r_{\rm H})$ in the presence of $HCo(CO)_4$, $Co(CO)_8$ and octene-1 in heptane solution under CO atmosphere at various conditions at 15 °C

Table VIII

* DCo(CO)4

Table IX

Initial CO absorption rates $(r_{\rm CO})$ and initial hydrogenation rates $(r_{\rm H})$ in the presence of $HCo(CO)_4$ and ethyl acrylate in octane solution at various $HCo(CO)_4$ concentrations and total pressures of CO at 10 °C

$r_{ m H} \cdot 10^6$ $(M \cdot s^{-1})$	$r_{\rm CO} \cdot 10^{6}$ ($M \cdot {\rm s}^{-1}$)	[CO] · 10 ² (M)	[Co ₂ (CO) ₈] (M)	$[\mathrm{HCo}(\mathrm{CO})_{4}]_{1}^{'}$ (M)
1.2	3.0	1.036	0.0168	0.0104
	3.62	1.020	0.0168	0.0140
7.0	5.1	0.424	0.0168	0.0208
	4.52	1.016	0.0168	0.0208
2.5	4.34	1.036	0.0168	0.0208
0.7	4.0	2.812	0.0168	0.0208
	5.40	1.020	0.0168	0.0290
7.1	6.10	1.036	0.0178	0.0417
13ª	13.24^{a}	1.036	0.0172	0.0436
	7.2	1.023	0.0168	0.0632
16	8.62	1.036	0.0178	0.0904

Initial concentration [ethyl acrylate] = 0.139 M

* [ethyl acrylate] = 0.269 M

The following discussion will be limited to olefins belonging to the first group, *i.e.* those which require $Co_2(CO)_8$ for their reaction with $HCo(CO)_4$.

The kinetics in the case of heptene-1⁺, octene-1⁺ and ethyl acrylate show that $\text{Co}_2(\text{CO})_8$ catalyzes not only the acylcobalt carbonyl formation, but the stoichiometric hydrogenation as well. Both reactions are of half order for $\text{Co}_2(\text{CO})_8$ and of first order for the olefin. (See Tables II, III, IV and V.) The reaction rates are not influenced by the diffuse light in the laboratory. The rate dependence on $\text{HCo}(\text{CO})_4$ and CO concentration (CO inhibits both



Fig. 2. The experimental carbonylation rate ($r_{\rm CO} = \text{mol CO/L/s}$) and hydrogenation rate ($r_{\rm H} = \text{mol saturated compd./L/s}$) ratios vs. [CO]/[HCo(CO)₄] plots

reactions) is more complex. (See Tables VI, VIII and IX.) The ratio of the rates of CO absorption $(r_{\rm CO})$ and hydrogenation $(r_{\rm H})$ is a function of [CO]/[HCo(CO)₄] as can be seen Fig. 2. This supports in a quantitative manner the widely accepted qualitative picture, deduced from both catalytic acid stoichiometric hydroformylations, that the ratio of hydrogenation vs. carbonylation increases with the HCo(CO)₄ concentration.

Using $DCo(CO)_4$ instead of $HCo(CO)_4$ there, is practically no kinetic isotope effect in carbonylation: $(r_{CO})_{HCo(CO)_4}(r_{CO})_{DCo(CO)_4} = 1.03 - 1.05$, but a medium effect was observed in hydrogenation: $(r_H)_{HCo(CO)_4}/(r_H)_{DCo(CO)_4} = 1.6 - 2.2$ (see Table VIII). Owing to the competing nature of the carbonylation and hydrogenation, with $DCo(CO)_4$ instead of $HCo(CO)_4$ we get more CO absorption and less octane, as can be seen in Table X.

⁺ Some of these results were published briefly [9]

Table X

The amounts of observed CO and octane formed in the reaction of $HCo(CO)_4$ and $DCo(CO)_4$ with octane-1 in the presence of $Co_2(CO)_8$ under CO in heptane solution at 15 °C. Total pressure: 99.0 \pm 0.4 kPa [Octane-1]₀ = 0.378 M, liquid volume: 1.68 mL, gas phase volume 54 mL, $[Co_2(CO)_8]_0 = 0.068 M$

Time (min)	HCo(CO), (mmol)	octane (mmol) ^a	CO abs. (mmol) ^b	DCo(CO), (mmol)	oc tane (mmol) ^a	CO abs. (mmol) ^b
0	0.815	0.000	0.000	0.800	0.000	0.000
180		0.223	0.183		0.209	0.227
370				0.00	0.227	0.256
420	0.00	0.252	0.210			

^a Determined, after quenching with pyridine, by GC analyses using nonane internal standard. Small amounts of nonanals and traces of nonanols were detected also corresponding to about 10% of HCo(CO)₄ or DCo(CO)₄ consumption

^b Measured using a gas burette

One of the possible mechanisms which fits the kinetic data is proposed below.*

$$\operatorname{Co}_{g}(\operatorname{CO})_{g} \stackrel{K_{1}}{\longleftrightarrow} 2 \cdot \operatorname{Co}(\operatorname{CO})_{4}$$
$$\cdot \operatorname{Co}(\operatorname{CO})_{4} + \operatorname{RCH} = \operatorname{CH}_{2} \stackrel{K_{3}}{\longleftrightarrow} \cdot \operatorname{Co}(\operatorname{CO}_{g})(\operatorname{RCH} = \operatorname{CH}_{2}) + \operatorname{CO}$$
$$\operatorname{Co}(\operatorname{CO})_{3}(\operatorname{RCH} = \operatorname{CH}_{2}) + \operatorname{HCo}(\operatorname{CO})_{4} \stackrel{k_{a}}{\xrightarrow{\operatorname{cov}}} \operatorname{HCo}(\operatorname{CO})_{3}(\operatorname{RCH} = \operatorname{CH}_{2}) + \cdot \operatorname{Co}(\operatorname{CO})_{4}$$

* Another possible mechanism which also fits the kinetic data is the following:

$$Co_{2}(CO)_{8} \stackrel{K_{1}}{\longleftarrow} 2 \cdot Co(CO)_{4}$$

$$HCo(CO)_{4} + \cdot Co(CO)_{4} \stackrel{K_{4}}{\longleftarrow} H\dot{C}o_{2}(CO)_{7} + CO$$

$$H\dot{C}o_{2}(CO)_{7} + RCH = CH_{2} \stackrel{K_{8}}{\longrightarrow} H\dot{C}o_{2}(CO)_{6}(RCH = CH_{2}) + CO$$

$$H\dot{C}o_{2}(CO)_{6}(RCH = CH_{2}) + CO \stackrel{k_{b}}{\Longrightarrow} RC_{2}H_{4}\dot{C}o_{2}(CO)_{7}$$

$$RC_{2}H_{4}\dot{C}o_{2}(CO)_{7}$$

$$RC_{2}H_{4}\dot{C}o_{2}(CO)_{7}$$

$$RC_{2}H_{4}\dot{C}o_{2}(CO)_{7} + \cdot Co(CO)_{4}$$

$$RC_{2}H_{4}CO\cdot Co_{2}(CO)_{7} - CO \stackrel{1}{||} + cO$$

$$RC_{2}H_{4}COCo(CO)_{4} + \cdot Co(CO)_{4} - Co \stackrel{1}{||} + cO$$

No clear evidence is available at present to distinguish between these two (and several other possible) mechanisms, which shows the limits of unambiguity attainable by kinetic methods for a reaction system as complex as the presently investigated one.

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Assuming steady state conditions for the alkylcobalt intermediates, the following rate expressions can be derived for the formation of RC₂H₄COCo(CO)₄ (Eq. 1) and RC_2H_5 (Eq. 2) if $[Co_2(CO)_8]$ and $[RCH=CH_2]$ are constant:

$$\frac{\mathrm{d}[\mathrm{RC}_{2}\mathrm{H}_{4}\mathrm{COCo(\mathrm{CO})_{4}}]}{\mathrm{d}t} = r_{\mathrm{CO}} = \frac{B\frac{k_{\mathrm{CO}}}{k_{\mathrm{H}}}[\mathrm{HCo(\mathrm{CO})_{4}}]}{\frac{k_{\mathrm{CO}}}{k_{\mathrm{H}}}[\mathrm{CO}] + [\mathrm{HCo(\mathrm{CO})_{4}}]}$$
(1)

$$\frac{\mathrm{d}[\mathrm{RC}_{2}\mathrm{H}_{5}]}{\mathrm{d}t} = r_{\mathrm{H}} = \frac{B[\mathrm{HCo}(\mathrm{CO})_{4}]^{2}[\mathrm{CO}]^{-1}}{\frac{k_{\mathrm{CO}}}{k_{\mathrm{H}}}[\mathrm{CO}] + [\mathrm{HCo}(\mathrm{CO})_{4}]}$$
(2)

$$B = A \cdot [\operatorname{Co}_2(\operatorname{CO})_8]^{0.5} [\operatorname{RCH} = \operatorname{CH}_2]$$
 $A = k_{\mathrm{a}} \cdot K_1^{0.5} \cdot K_2^*$

and

where

The kinetic constants
$$A$$
 and $\frac{k_{\rm CO}}{k_{\rm H}}$ may be determined by transforming

Eq. (1) into Eq. (3)

$$\frac{1}{r_{\rm CO}} = \frac{[\rm CO]}{B[\rm HCo(\rm CO)_4]} + \frac{1}{B\frac{k_{\rm CO}}{k_{\rm H}}}$$
(3)

and plotting $\frac{1}{r_{CO}}$ against $\frac{[CO]}{[HCo(CO)_4]}$. This is shown in Figs 3, 4 and 5 for

different olefins.

* or $A = k_b \cdot K_1^{0.5} \cdot K_4 \cdot K_5$.

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Fig. 3. The reciprocal initial rate of CO absorption $(1/r_{CO})$ vs. $[CO]/[HCo(CO)_4]$ at 15 °C in heptane solution under CO between 0.5 and 3 bar total pressure; [heptene-1] = 1.02 M; $[Co_2(CO)_8] = 0.072 M$; [octene-1] = 0.050 M; (o) experiments using DCo(CO)_4



Fig. 4. The reciprocal initial rate of CO absorption $(1/r_{CO})$ vs. $[CO]/[HCo(CO)_4]$ at 15 °C in octane solution under atmospheric pressure of CO; $[heptene-1] = 0.157 \ M$, $[heptene-2]^a = 0.690 \ M$, $[heptene-3]^b = 0.715 \ M$, $[Co_2(CO)_8] = 0.048 \ M$ ^a Mixture of 47% trans and 53% cis, ^b Mixture of 30% trans and 70% cis



Fig. 5. The reciprocal initial rate of CO absorption $(1/r_{\rm CO})$ vs. $[\rm CO]/[\rm HCo(\rm CO)_4]$ at 10 °C in octane solution under CO between 0.5 and 3 bar total pressure; [ethyl acrylate] = 0.139 M, $[Co_2(CO)_8] = 0.0168 M$

Table XI

[olefin] (M)	$\frac{k_{\rm CO}}{k_{\rm H}}^{\rm c}$	$\frac{k_{\rm CO}}{k_{\rm H}}^{\rm d}$	
heptene-1	0.157	21	16
heptene-1	1.02		19
octene-1	0.10	12	15.6
trans-heptene-2	0.715	12.3	
heptene-2 ^e	0.690		8.4
trans-heptene-3	0.715	6.5	
heptene-3 ^t	0.715		13.8
cyclohexene	1.97		10.6
ethyl acrylate	0.139	4.2 ^g	3.6 ^g

The ratio of rate constants k_{CO}/k_H for some olefins at 15 °C calculated from the experimental rates of carbonylation^{*} and hydrogenation^b compiled in Tables I, VI, VIII and IX

* $r_{\rm CO}$ in mol CO absorbed/L/s ^b $r_{\rm H}$ in mol saturated compound formed/L/s ^c Calculated as $k_{\rm CO}/k_{\rm H} = r_{\rm CO}[\rm HCo(\rm CO)_4]/r_{\rm H}[\rm CO]$ ^d Calculated from $1/r_{\rm CO} = [\rm CO]/B \cdot [\rm HCo(\rm CO)_4] + 1/B \ k_{\rm CO}/k_{\rm H}$ plots [see Eq. (3)] where $B = A \cdot [\rm Co_2(\rm CO)_8]^{0.5}$ [olefin] ^e Mixture of 47% trans and 53% cis ^f Mixture of 30% trans and 70% cis ^g At 10 °C

g At 10 °C

Dividing Eq. (1) by Eq. (2) we obtain Eq. (4):

$$\frac{r_{\rm CO}}{r_{\rm H}} = \frac{k_{\rm CO}}{k_{\rm H}} \cdot \frac{[\rm CO]}{[\rm HCo(\rm CO)_4]} \tag{4}$$

which makes possible the calculation of the $k_{\rm CO}/k_{\rm H}$ values in another way from the experimentally observed rates.

Table XI compiles the values of $k_{\rm CO}/k_{\rm H}$ determined for different olefins. As can be seen, this value decreases in the order hydrocarbon α -olefins > hydrocarbon inner olefins > ethyl acrylate. This is in agreement with the general experience that hydrogenation as a side reaction increases in this order in catalytic hydroformylation with $\operatorname{Co}_2(\operatorname{CO})_8$ [1].

An increase in temperature also favour $r_{\rm H}$ over $r_{\rm CO}$ (see Table XII), again an observation which is in accordance with the catalytic experiments [1]. Both concordances support the conclusion that the same chemistry is operating under our stoichiometric and the industrial catalytic conditions.

Table XII

The temperature dependence of the carbonylation and hydrogenation rates Initial concentrations: [ethyl acrylate] = $0.139 \ M$, [Co₂(CO)₈] = $0.0168 \ M$, [HCo(CO)₄] = $0.0208 \ M$

Temp. (°C)	[CO] · 10* (M)	$r_{\rm CO} \cdot 10^6$ $(M \cdot s^{-1})$	$r_{\mathbf{H}} \cdot 10^{6}$ ($M \cdot \mathrm{s}^{-1}$)	$\frac{k_{\rm CO}}{k_{\rm H}}$ a
5	1.010	2.86	1.3	4.5
10	1.036	4.34	2.5	3.6
15	1.072	6.53	4.8	2.6
20	1.098	9.60	9.5	1.9
25	1.128	14.5	17	1.6

Initial concentrations: [heptene-1 = 0.1567 M, [Co₂(CO)₈] = 0.048 M, [HCo(CO)₄] = 0.0292 M

Temp. (°C)	[CO] · 10 ^a (M)	$r_{ m CO} \cdot 10^{6}$ $(M \cdot s^{-1})$
10	1.055	1.21
15	1.097	2.21
20	1.143	4.35
25	1.176	7.98
30	1.205	14.5

* Calculated as $k_{\rm CO}/k_{\rm H} = r_{\rm CO} \ [{\rm HCo(CO)_4}]/r_{\rm H} [{\rm CO}]$

*

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ALKYLCOBALT TETRACARBONYLS, Va

REACTION OF α -SUBSTITUTED α -HALOACETIC ACID ESTERS WITH Na[Co(CO)₄]^b

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 α -Substituted α -bromoacetic acid exters, RBrCHCOOR' (R=Me, t-Bu, Ph, COOEt; R'=Me, Et) were made to react with Na[Co(CO)₄]. The corresponding alkylcobalt tetracarbonyls, and with PhBrCHCOOEt also the π -benzylcobalt tricarbonyl derivative, could be detected by IR spectroscopy. The organic decomposition products of the intermediate organocobalt compounds indicate radical reaction pathways.

Introduction

It is known that alkyl halides react with the tetracarbonylcobaltate anion yielding alkylcobalt tetracarbonyls. It appeared obvious to extend this reaction to alkyl halides containing functional groups in the alkyl rest. In the last two decades attempts have been made at achieving the reaction of α -haloacetic acid derivatives with $[Co(CO)_4]^-$; however the early efforts produced little information.

The first studies detected only that reaction takes place [6], but the products could not be identified. Subsequent research dealt mainly with the organic products.

TAKEGAMI et al. [7, 8] allowed K [Co(CO)₄] to react with α -bromopropionic acid ester and obtained indirect indication of the formation of the corresponding — and β -cobalt carbonyl alkyl- and acyl derivatives. The main conclusion drawn by these authors was a hypothesis of the $\alpha \rightarrow \beta$ isomerization of the primary α , β -(tetracarbonylcobalt)propionic acid ester. This supposition was based on the gas chromatographic detection of the corresponding methylmalonic and succinic acid esters obtained by decomposition with I₂/tolueneethanol (7.5:1) reagent.

The THF solution of $\text{Co}_2(\text{CO})_8$ (which might have contained $[\text{Co}(\text{THF})_8]$ $[\text{Co}(\text{CO})_4]_2$, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ under the conditions used) was made to react [9] with methyl D, L- and D-bromophenylacetate, as well as with dimethyl bromomalonate. Products of a coupling reaction occurring at the α -carbon

^a For Parts I-IV, see Refs [1-4]

^b Preliminary results were presented in a Note [4] and at a Conference [5]

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atom were isolated and identified in 20-40% yields. SEYFERTH and MILLAR [9] considered the possibilities of polar (S_Nl type, perhaps with the intermediacy of π -benzyl and/or π -oxapropenyl type organometallic species), or radical reaction routes.

Recently we succeeded in preparing stable $(CO_4)CoCH_2COOR$ compounds from haloacetic acid esters and sodium tetracarbonyl cobaltate in almost quantitative yields [2, 3]. It was logical to continue these studies by a systematic investigation of the reaction of α -substituted α -haloacetic acid esters with Na[Co(CO)₄].

Results and Discussion

Solutions of Na[Co(CO)₄] prepared were in Et₂O and allowed to react with RBrCHCOOR' (R= Me, t-Bu, Ph, COOEt; R' = Me, Et) at $-50 \degree$ C to room temperature. The colourless solution became almost immediately (1-5 min) brownish-red, and a white solid (NaBr) precipitated.

These reaction mixtures were analyzed by the following methods.

(a) The solvent was drawn off (at low temperature), the residue extracted with *n*-hexane, and infrared v(C-O) spectra were taken as quickly as possible (Table I).

Table I

 $\nu(C-O)$ Spectra of RCH(COOR')Co(CO)₄ (R = Me, R' = Et; R = Ph, R' = Me) compounds Solvent: n-hexane; values in cm⁻¹

Compound	v(C-O) terminal	v(C-0) ester in complex
CH ₃ CH(COOEt)Co(CO) ₄	2107.9 m; 2041.4 s;	
	2031.9 vs; 2021.4 vs	1715 w
PhCH(COOMe)Co(CO) ₄	2105.5 m; 2040.5 s;	
	2031 vs; 2025 sh	1715 w
η ³ -[PhCH(COOMe)]Co(CO) ₃	2064.0 s; 2006.0 s;	
	1990.5 s	

(b) Decomposition with I_2/ROH (R = Me, Et), followed by subsequent GC/MS analysis of the organic products.

(c) In the case of the R=Ph reaction with $HCo(CO)_4$, as described in Ref. [2].

The spectroscopic analysis of the organocobalt product was complicated by the fact that the reaction mixtures generally contained more than one

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substance. Using, however, substraction of the spectra, the presence of the corresponding alkylcobalt tetracarbonyls could be detected undoubtedly for the R=Me and Ph and very probably, for the R=t-Bu derivatives. No indication of the presence of a β -metallated derivative (isomerization product according to Refs [7, 8]) was obtained in the reaction with α -bromopropionic acid ethyl ester. Considerable amounts, generally exceeding that of the alkyls, of Co₂(CO)₈ were always present. In the R=Ph derivative a π -allyl type complex was detected, which was absent in the other experiments; this allows the assignment of a π -benzylcobalt tricarbonyl, rather than a π -oxallyl, structure to this compound. The results can thus be depicted as shown in Scheme 1.



The decomposition of the reaction mixtures yielded $\sim 5-10\%$ unchanged starting material, hydrogenated and carbonylated derivatives, along with coupling products of the starting compounds. When R=Me, the decomposition products, were almost exclusively propionic and acrylic acid esters if oxygen had been very cautiously excluded. Under less rigorous anaerobic conditions the amounts of these products markedly decreased, and methylmalonic and succinic acid esters (as reported also by previous workers [7, 8]) appeared. The formation of acrylic acid ester provides a piece of evidence for a β -H-elimination reaction route as supposed formerly [10].

The reaction with t-BuCHBrCOOEt gave predominant formation of the hydrogenated derivative, and a smaller amount of the coupled (*meso-* and D,L-*di-t*-butyl succinic acid ester) and carbonylated (t-Bu-malonic acid ester) products.

The reaction of α -bromophenylacetic acid ester presented a most multifarious organic chemistry. Here again 10-30% hydrogenated phenylacetic acid ester and 10-30% carbonylation product (phenylmalonic acid ester) were found; about two-thirds of the products can be deduced from C-C coupling reactions. In the latter category not only the *meso-* and racemic diphenylsuccinic acid esters (reported by SEYFERTH and MILLAR [9]) but also products of coupling of aromatic ring vs. aliphatic carbons could be detected in 15-30%.

Treatment of the reaction mixture with $HCo(CO)_4$ yielded similar products as decomposition by the I_2/ROH reagent, with two important differences: (i) the relative amount of the hydrogenated product increased, and (ii) any carbonylation product was absent.

The effect of the atmosphere (argon or carbon monoxide) in this reaction was also studied (Table II). The most striking result of these experiments

Conditions	С	0	Ar/	со	· .	Ar	Cross coupling with
Product	—20 °C	—50 °C	—20 °C	—50 °C	—20 °C	—50 °C	BrCH(COOEt), —30 °C/CO
Ph-CH ₂ COOMe	26.25	28.21	26.73	25.99	15.28	15.90	39.07*
Ph-CH(COOMe) ₂	15.15	20.71	18.26	22.34	30.19	34.56	32.34
(PhCHCOOme) ₂ meso racemic	$\begin{array}{c} 20.28\\ 9.84\end{array}$	$\begin{array}{c} 14.96\\9.55\end{array}$	$\begin{array}{c} 20.66\\ 10.06\end{array}$	$\begin{array}{c} 19.28\\ 15.76\end{array}$	$\begin{array}{c} 18.97\\ 20.40\end{array}$	$\begin{array}{c} 19.75\\ 22.04 \end{array}$	9.29 9.64
CH ₂ -COOMe CH-COOMe	15.80	12.37	16.03	11.09	8.63	4.50	4.45
CH ₂ -COOMe	12.27	14.20	8.26	5.55	6.52	3.26	5.20

Table II

Distribution of the organic products in the reaction of $Na[Co(CO)_4]$ with PhCh(Br)COOMe (in relative mole%)

* From the bromomalonic ester only the hydrogenated product, CH₂(CCOEt)₂ was formed.

has been that the relative weight of the carbonylated product is significantly higher in Ar than under CO. The D, L/meso ratio of the diphenylsuccinic acid esters shows also a dramatic change from 1:1 (Ar) to 2:1 (CO). Consumption of CO by the reaction mixture before decomposition could not be detected

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with certainty; at the relatively low temperatures used, this is, at any rate, difficult to measure. Temperature has no significant effect on the preparative results, at least, not in the range of -50 to -20 °C.

These results indicate different mechanisms operating in the decomposition. A purely radical pathway seems to be the most probable under Ar, and a competition between this and other parallel route(s) under CO atmosphere. Scheme 2 shows a possible interpretation of these findings.





In the reaction with bromomalonic acid ester, the hydrogenated malonic acid ester was found to be the almost exclusive main product, along with some unidentified minor components.

It was attempted to achieve a "cross coupling" reaction between bromophenylacetic acid and bromomalonic acid esters. No detectable quantity of cross-coupled product was observed; the only interesting feature of this reaction was a noteworthy increase in the relative amount of the hydrogenated and carbonylated products. This observation provides a further hint at the possibility of geminate radical pair mechanisms, as proposed both for cobaltassisted stoichiometric hydrogenation [11-16] and carbonylation [11, 15, 18] of olefins.

The analysis of the organic products allows some further conclusions.

(i) Under the reaction conditions used, the formation of the hydrogenated and coupling products hints at the participation of radical pathways of transformation of the primary alkylcobalt tetracarbonyls (and π -benzylcobalt tricarbonyl). The radical decomposition seems to start at a rate comparable with (or for R = COOR' even higher than) the reaction of the organic halide and Na[Co(CO)₄].

(*ii*) It is interesting to note that starting from $CH_3Co(CO)_4$ and changing (formally) a hydrogen atom for an electronegative polar substituent (F [17], Ph [18], CN [6b] or COOR' [2-4]), the stability of the alkyl markedly increases and CO "insertion" becomes more difficult, or even practically impossible, whereas when changing one H for an electron-releasing group such as Me[6b, 19] or Et [20], the stability is not markedly altered, neither is the tendency for CO "insertion".

The exchange of one more or two H atoms for fluorine increases the stability and the tendency for insertion is again absent [17].

Two or three alkyl groups seem to have qualitatively similar influence as one alkyl has [6, 19–22].

Taking one electronegative substituent (as in the present work COOR'), the stability is definitely decreased by the presence of either an electron donor (Me, t-Bu) or an electron acceptor (Ph, COOR') group, while the tendency for CO insertion is observable only for Me [7, 8] and Ph* substituents; even in these cases only to a limited extent.

All these observations indicate a large diversity in the interactions of these substituted methyl groups with the $Co(CO)_4$ rest in the corresponding alkylcobalt carbonyls^{**}. Similarly, a large substitutent effect in the reaction rates, mechanism weights, as well as in the stability and reactivity of the eventually formed organic radicals can be expected. Recent kinetic studies [15, 16] on the stoichiometric hydroformylation of various olefins seem to be in agreement with the above argumentation.

(*iii*) The presence of the aromatic ring-coupled products in the case of PhCHBrCOOEt displays multifold interest.

(a) This observation furnishes a further indication of the presence of the π -benzyl (and not π -oxapropenyl) type intermediate.

^{*} Independence of the yield of the carbonylated product from the atmosphere with PhCHBrCOOEt suggest that carbonylation was an instantaneous side reaction of the decomposition.

^{**} Preliminary results of an Extended Hückel/Wolfsberg-Helmholz MO study [23] support this view.

(b) Formation of the *para* isomer provides further indirect evidence for the presence of on-the-ring radicals in the reaction.

(c) The sharp dependence of the relative weight of the ring-coupled products on the atmosphere is a challenging feature of the reaction, but it can hardly be explained on the basis of the rest of the evidence.

Experimental

The organic halides used in this study were commercial products or were prepared by standard literature procedures. The ether and THF were passed through a column of activated alumina to remove peroxides, then distilled from sodium wire under argon. They were stored under argon in the dark. Benzene and CCl₄ were dried over P_2O_5 . Dicobalt octacarbonyl was made by literature procedures [24]; it was recrystallized from dichloromethane.

The reactions were carried out in a Schlenk-type tube under an atmosphere of purified argon or carbon monoxide.

The infrared spectra were recorded with an IR-75 (Carl Zeiss, Jena) double-beam spectrophotometer. The calibration of the IR spectra was effected by the subsequent recording of a CO gas spectrum. ¹H-NMR spectra were recorded with a BS-487 (Tesla, Brno, CSSR) 80 MHz instrument and mass spectra with a IMS 01 SG-2 (JEOL) mass spectrometer. The organic samples were analyzed by a HP 5830 A gas chromatograph, using a 10-m long SE-30 glass capillary column.

Reactions of Na[Co(CO)₄] with α -halocarboxylic acid esters

(a) α-Bromopropionic acid ethyl ester

A solution of 0.67 mmol of Na[Co(CO)₄] in 10 mL of ether was treated with 121 mg (86 μ L 0.67 mmol) of α -bromopropionic acid ethyl ester at 20° under CO. The solution turned dark-red almost immediately and no gas volume change was observed. After 6 h, 0.26 g of I₂ (1 mmol) and 1 mL of EtOH were added. When the gas evolution ceased, the dark-green solution was washed with 10 mL of 5% Na₂S₂O₃, and with water, then dried over Na₂SO₄ and analyzed by GC/MS. Ethyl acrylate (0.14 mmol) and ethyl propionate (0.38 mmol) were found, identified by their mass spectra.

If the reaction was carried out under less rigorous anaerobic conditions (which was indicated by the pale red colour of the starting $Na[Co(CO)_4]$ solution) 0.12 mol of ethyl acrylate, 0.26 mol of ethyl propionate, 0.17 mol of diethyl methylmalonate and 0.44 mol of diethyl succinate per mole of cobalt were formed and identified after the decomposition.

(b) α-Bromo-t-butylacetic acid ethyl ester

Two mmol of Na[Co(CO)₄] in 30 mL of ether and 424 mg of t-BuCH(Br)COOEt were refluxed under CO. The solution turned violet and finally greenish-brown. After 1.5 h only Co₄(CO)₁₂ was detected as the organometallic product (by IR spectroscopy) in the solution. The mixture was treated with I_2 /EtOH and the solvent was evaporated. The residual oil was taken up in 10 mL of CCl₄ and after washing (5% Na₂S₂O₃, water) and drying analyzed by GC. Besides several minor components (less then 0.5%) 85.7% t-BuCH₂COOEt, 11.7% starting bromocompound, 1.58% carbonylated product t-BuCH(COOEt)₂ and 0.82% (t-BuCHCOOEt)₂ were found and identified by their mass spectra.

(c) Esters of *a*-bromophenylacetic acid

A solution of 0.34 g (1 mmol) of $\text{Co}_2(\text{CO})_8$ in 30 mL of Et_2O was added to 40 g of 1.5% sodium amalgam. The mixture was stirred at room temperature under carbon monoxide until a colourless solution was obtained. This was allowed to stand for 30 min and then transferred to the reaction vessel, cooled to -20 - 50 °C, and treated with a solution of 1.9 mmol of PhCH(Br)COOR (R=Me, Et) under argon or CO. The solution turned brownish-red almost

immediately. After 1 h 0.51 g (2 mmol) of I_2 and 2 mL of ROH (R=Me, Et) were added. Vigorous gas evolution occurred and the colour of the solution changed to dark-green. The mixture was let to warm up, and the solvent was evaporated at room temperature under reduced pressure. The residual oil was taken up in 10 mL of CCl₄, the brown solution was washed with 20 mL of 5% Na₂S₂O₃, water, dried over Na₂SO₄ and a small part was analyzed by GC and MS. The solution was concentrated to 2 mL and the main products were isolated by preparative GC (3 m long, 15% neopentyl glycol succinate column). ¹H-NMR spectra were recorded in CCl₄ solution (Table III).

Compound	∂TMS (ppm, CCl₄)	Assignment
$\mathrm{PhCH}_{2}\mathrm{COOCH}_{2}\mathrm{CH}_{3}$	1.04, t, 3H 3.35, s, 2H 3.91, q, 2H 7.01, m, 5H	$\begin{array}{c} \mathrm{CH}_2 - \mathrm{CH}_3 \\ \mathrm{Ph} - \mathrm{CH}_2 - \mathrm{COO} \\ \mathrm{O} - \mathrm{CH}_2 - \mathrm{CH}_3 \\ \mathrm{Ph} \end{array}$
PhCH(COOCH ₂ CH ₃) ₂	1.12, t, 6H 4.04, q, 4H 4.29, s, 1H 7.02, m, 5H	$\begin{array}{c} \mathrm{CH}_2 - \mathrm{C}H_3\\ \mathrm{O} - \mathrm{C}H_2 - \mathrm{CH}_3\\ \mathrm{Ph} - \mathrm{C}H - (\mathrm{COO})_2\\ Ph \end{array}$
$\begin{array}{c} meso \ + \ \mathrm{racemic} \\ \mathrm{Ph-CH-COOCH_2CH_3} \\ \mathrm{I} \\ \mathrm{Ph-CH-COOCH_2CH_3} \end{array}$	$\begin{array}{cccc} 0.73, & t, 3H \\ 1.05, & t, 3H \\ 3.78, & m, 6H \\ 7.08, & m, 10H \end{array}$	$\begin{array}{c} \mathrm{CH}_2 - \mathrm{C}H_3 \\ \mathrm{CH}_2 - \mathrm{C}H_3 \\ \mathrm{C}H + \mathrm{C}H_2 \\ Ph \end{array}$
CH ₂ -COOCH ₂ CH ₃ CH-COOCH ₂ CH ₃	$\begin{array}{c} 1.10, \mathrm{m}, 6\mathrm{H} \\ 3.43, \mathrm{s}, 2\mathrm{H} \\ 3.95, \mathrm{m}, 4\mathrm{H} \\ 5.14, \mathrm{s}, 1\mathrm{H} \\ 7.09, \mathrm{s}, 9\mathrm{H} \end{array}$	$\begin{array}{c} \mathrm{CH}_2-\mathrm{C}H_3\\ \mathrm{C}H_2-\mathrm{Ph}\\ \mathrm{C}H_2-\mathrm{CH}_3\\ \mathrm{C}H\\ \mathrm{Ph} \end{array}$
CH ₂ -COOCH ₂ CH ₃	1.11, dt, 6H 3.34, s, 2H 3.98, q, 4H 4.71, s, 1H 7.09, d, 9H	$\begin{array}{c} \mathrm{CH_2-CH_3}\\ \mathrm{CH_2-Ph}\\ \mathrm{CH_2-CH_3}\\ \mathrm{CH}\\ \mathrm{Ph} \end{array}$

Т	a	b	le	П	T
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(d) Diethyl bromomalonate

The reaction of 2 mmol of $Na[Co(CO)_4]$ (prepared as above) with 1.9 mmol of diethyl bromomalonate was carried out under similar conditions. After the usual work-up of the reaction mixture, the resulting solution was analyzed by GC-MS. Besides several minor

components (less than 0.5%) only the product of hydrogenolysis, diethyl malonate, was found. No "coupling" product, tetracarboethoxyethane, was obtained.

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CHEMICAL BASIS OF SPECTROPHOTOMETRIC DETERMINATION OF CYANAMIDE WITH PENTACYANOFERRATES

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The colour reaction between pentacyanoammineferrate(II) and cyanamide has been studied. It was found that an oxidizing agent is needed for the development of the colour. The reaction product was isolated and characterized as $Na_3Fe(CN)_5NCNH \cdot 3 H_2O$. In the direct reaction between cyanamide and pentacyanoammineferrate(III) an accelerating effect of pentacyanoammineferrate(II) was observed. Based on these results, a new method has been developed for the determination of cyanamide, using the mixture of pentacyanoammineferrate(III) and (II) as reagent and catalyst, respectively. Furthermore, this reaction was applied for the spectrophotometric determination of oxygen dissolved in water. The possibility of the determination of some guanidine and urea derivatives is discussed.

Introduction

The reaction between pentycyanoammineferrate(II) and cyanamide was first described by BAUDISCH [1], briefly mentioned by FEARON [2], and first applied for the determination of cyanamide by BUYSKE and DOWNING [3]. In these papers the reaction was described by the following equation:

 $Fe(CN)_5H_2O^{3-} + HNCN^- \rightarrow Fe(CN)_5NCNH^{4-} + H_2O$

In aqueous solution pentacyanoammineferrate(II) reacts as the pentacyanoaquaferrate(II) complex. It was found by BUYSKE and DOWNING [3] that neither oxygen nor light influence the reaction, in contrast with FEARON's results [2]. FEARON reported that development of the colour was faster when the reagent pentacyanoammineferrate(II) solution was exposed to light, or $S_2O_8^{2-}$ as oxidizing agent was added. A role of pentacyanoaquaferrate(III) was assumed, but was not proven. For determination of some other substrates with pentacyanoammineferrate(II), NO_2^{-} was suggested by LARUE [4] as oxidizing agent without dealing with its effect in detail. Later MUSHKIN [5] described a cyanamide determination in which pentacyanonitrosylferrate(II) was used as reagent and the catalytic effect of hexacyanoferrate(III) was found.

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In the above three references [2, 4, 5] not even stoichiometric equations were given.

Recently NIEMAN et al. [6] published a kinetic method for determination of cyanamide using the reaction. In contrast with earlier work [1-3], the stoichiometry of the reaction was described as 2:1 = complex: cyanamide [7]. The calculated molar absorptivity of the coloured product at 530 was found to be 2850 $M^{-1} \text{ cm}^{-1}$ [7], which differs significantly from the $\varepsilon = 3500$ $M^{-1} \text{ cm}^{-1}$ estimated from data of ref. [3]. For explanation of the kinetic results the pK₁ of cyanamide, defined by the equation:

$$H_2NCN \rightleftharpoons HNCN^- + H^+$$

was used as 1.1. In fact this pK corresponds to the equilibrium

$$H_2NCN + H^+ \rightleftharpoons H_3NCN^+$$

and was determined by SOLOWAY and LIPSCHITZ [8]. However, when repeating the mole ratio experiments of refs [6, 7], we observed that the absorbances depended on the ageing of pentacyanoammineferrate(II) solution, causing a lack of reproducibility. We suspected that the oxygen content of the reagent solution was responsible for this and the experiments were repeated under argon atmosphere. In this way colourization was not observed, but the colour developed on addition of an oxidizing agent (e.g. H_2O_2) or upon bubbling air through the solution. The final absorption spectrum was identical with the spectrum reported by BUYSKE and DOWNING [3].

These facts urged us to investigate the nature of this reaction in order to improve the analytical procedure.

Experimental

Apparatus

The visible and infrared spectra were recorded with Beckman Acta III and Perkin-Elmer 283 B spectrometers. The kinetic measurements were carried out with a home-made rapid mixing apparatus combined with a Hitachi Perkin-Elmer 139 spectrophotometer (optical path 8 mm). Magnetic measurements were run on a Jeol JMM-100 NMR spectrometer in aqueous solution (9). The Mössbauer spectra were obtained with an apparatus constructed at the Department of Atomic Physics of Loránd Eötvös University, Budapest.

Reagents

 $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$ and $Na_2Fe(CN)_5NH_3 \cdot H_2O$ were prepared according to the literature [10]. The iron and sodium contents of the complexes were determined by atomic absorption spectroscopy and flame photometry, using $Na_2Fe(CN)_5NO \cdot 2H_2O$ (Reanal) as standard. Fluka cyanamide (stabilized with 2% boric acid) was used without further purification. The concentration was determined by argentometric titration [6], using KI solution and a iodide selective electrode (Radelkis OP-I) for end-point indication.

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Procedure

The mole ratio experiments were carried out with pentacyanoammineferrate(III) in the usual way. The absorbances were measured after 10 hours. The calibration curves were obtained with a mixture of pentacyanoammineferrate(II) and (III), the concentrations being $0.01 \ M$ and $0.001 \ M$, respectively. Absorbances were measured after $5-10 \ min$ at 530 nm using 1 cm glass cells, against the same solutions without cyanamide. All these measurements were carried out at pH = 10.5 (borate buffer). A similar method was followed in the case of the other compounds studied.

Preparation of the product: 0.4 g cyanamide and 0.4 g $Na_2Fe(CN)_5NH_3 \cdot 3 H_2O$ were stirred in 100 mL methanol and 1 mL 30% aqueous H_2O_2 was added to this mixture. After two hours, the unreacted complex was filtered off. From the purple filtrate the product was precipitated with ether and dried in air.

Determination of oxygen dissolved in water: a $10^{-2} M$ pentacyanoferrate(II) solution containing $10^{-3} M$ HCl and a cyanamide solution $(10^{-2} M, \text{pH} = 10.5 \text{ adjusted})$ with borate buffer) was kept under argon atmosphere. A saturated aqueous solution of oxygen was prepared $(1.25 \times 10^{-3} M [11])$ at atmospheric pressure, and different volumes of it were injected into the optical cells (closed with a septum), which were previously flushed with argon. The samples were filled up to 1 mL with oxygen-free water and 0.5 mL pentacyanoammineferrate(II) solution were injected into them. After $2-3 \min$, 2 mL portions of the cyanamide solutions were injected into the samples and after 5 min the absorbances were measured at 530 nm using the same solution as reference without oxygen.

Results and Discussion

In contrast with the results of BUYSKE and DOWNING [3] we did not find any reaction in the absence of oxygen. When the kinetic experiments of NIEMAN *et al.* [6] were repeated, it was observed that the profiles of the kinetic curves, consequently, the initial rates too, depended on the ageing of pentacyanoammineferrate(II) solution kept in dark but without excluding the presence of air (Fig. 1). These curves indicate that this method is unsuitable for analytical application. Considering these observations it can be concluded



Fig. 1. Shape of kinetic curves depending on the ageing of pentacyanoammineferrate(II) solution. (1) 10, (2) 65, (3) 145, (4) 235, (5) 365, (6) about 2000 min. Concentration of cyanamide: $9 \times 10^{-5} M$, iron(II) complex: $2 \times 10^{-3} M$



Fig. 2. Accelerating effect of pentacyanoammineferrate(II). Concentration of iron(III) complex: 2×10^{-3} M, cyanamide: 9×10^{-5} M, iron(II) complex: (0) 0.0, (1) 4.0, (2) 8.0, (3) 12.0, (4) 16.0, (5) 20.0 $M \times 10^{-4}$

that it is the pentacyanoaquaferrate(III), formed by oxidation of pentacyanoaquaferrate(II), which is responsible for the colour reaction. Curve 6 in Fig. 1 shows that after 20 hours ageing the rate of colourization decreased despite the fact that the concentration of the iron(III) complex increased. It follows that the iron(II) content influences the reaction. Therefore, the reaction between cyanamide and pentacyanoammineferrate(III) in the absence and presence of pentacyanoferrate(II) under argon has been studied. (In fact, it is very difficult to prepare the pure iron(III) complex free from some iron(II) species but this does not influence our qualitative conclusions.)

The absorbance vs. time curves are shown in Fig. 2. Curve 0 shows the change of the absorbance without pentacyanoferrate(II). Curves 1-5 demonstrate that pentacyanoferrate(II) accelerates the reaction between cyanamide and the iron(III) complex. The induction periods in the curves indicate a multistep reaction mechanism.

The mole ratio experiment suggest a 1 : 1 complex formation (Fig. 3). The reaction product was isolated and analyzed for elements. C = 20.25%(20.5%), N = 26.7% (27.9%), H = 1.15% (2.0%), Fe = 15.2% (15.9%), Na = 19.1% (19.7%) were found, the calculated values for Na₃Fe(CN)₅NCNH · · 3 H₂O are in parentheses.

The results of structural investigation can be seen in Table I. The paramagnetic behaviour, the negative Mössbauer isomer shift and the large quadrupole splitting show that the central ion is a low-spin Fe³⁺ [12]. The IR streching frequency of coordinated cyanamide ($\nu NC \equiv N$) is shifted to lower wavenumbers. The $\nu NC \equiv N$ of the free ligand is 2210–2250 cm⁻¹ and that of the

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Fig. 3. The mole ratio curve. Concentration of cyanamide: $2 \times 10^{-4} M$

conjugated base is 2150 cm^{-1} [13]. This shift indicates the deprotonation and formation of a carbodiimide-like structure of the coordinated ligand [13].

An accelerating effect of pentacyanoferrate(II) ions in the substitution reactions of pentacyanoaquaferrate(III) with N_3^- and SCN⁻ has been observed and discussed by JAMES *et al.* [14]. Analogously, we suggest to describe the reaction by the following equations:

Mössbauer		
isomer shift	-0.30 mm s^{-1}	
quadrupole splitting	3.42 mm s^{-1}	
Magnetic moment	1.93 BM	
Infrared frequency		
$\nu NC = N$	2060 cm^{-1}	
visible spectrum		
λ_{\max}	530 nm	
$\varepsilon_{\lambda_{\max}}$	3530 s.dev. 22.1	

Table I															

Characteristics of the isolated reaction product

$$\begin{split} \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{H}_{2}\mathrm{O}^{3-} + \mathrm{HNCN}^{-} &\rightarrow \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{NCNH}^{4-} + \mathrm{H}_{2}\mathrm{O}\\ \\ \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{NCNH}^{4-} + \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{H}_{2}\mathrm{O}^{2-} &\rightarrow \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{NCNH}^{3-} + \mathrm{Fe}(\mathrm{CN})_{5}\mathrm{H}_{2}\mathrm{O}^{3-} \end{split}$$



Fig. 4. Calibration curves for determination of cyanamide (1-530 nm) thiourea (2-600 nm)and semicarbazide (3-505 nm)

We have found that these results -viz. the oxygen effect and the catalytic effect of iron(II) complex — were equally valid for some other organic compounds. The colours and the optimal pH values are summarized in Table II. It seems that the colour reactions with pentacyanoammineferrate(II) in the series of the ligands tested are rather exceptional, only nitrosobenzene and the phenylhydroxylamine form coloured complexes in the absence of oxygen. Two different colours were observed in the case of organic compounds containing both sulfur and nitrogen. This may be attributed to S and N donor isomers, however, no structural investigations were carried out.

On the basis of these observations, a reliable spectrophotometric method could be developed for the determination of cyanamide. The calibration curve is shown in Fig. 4. The relative standard deviation for three measurements is less than 2%. To indicate the possibility of the analytical application of this method for other compounds in Table II, calibration curves are shown for semicarbazide and thiourea too, in Fig. 4. (The determination of thiourea has also been suggested with light- "activated" pentacyanoamineferrate(II) [15].)

The observed effect of oxygen gives a possibility for its determination in aqueous solution spectrophotometrically. It has been reported by TOMA [16] that pentacyanoaquaferrate(II) reacts rapidly with oxygen in moderately acidic medium in the presence of trace amounts of transition metal ions (e.g. Fe^{2+} , which is readily freed from the complex by photodegradation). The pentacyanoferrate(III) formed is easily detectable with cyanamide spectrophotometrically. In Fig. 5, a calibration curve is shown for the determination

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Table II

Colour reactions of some organic compounds with pentacyanoammineferrate(II) and oxygen

Compound	Colour	Note
Guanidine	orange	$\mathrm{pH}=12$
Dicyandiamide	purple	$\mathrm{pH}=12$
Arginine	red	$\mathrm{pH}=12$
Semicarbazide	red	pH = 7 - 8
Urea	red	0.1 M NaOH
N-Hydroxyures	red	pH = 8-9
Histidine	red	$\mathrm{pH}=7\mathrm{-8}$
Thiourea	blue purple	$0.2~M~{ m acetic}~{ m acid}~{ m pH}=8\!-\!10$
Thiosemicarbazide	blue red	$0.01~M~{ m HCl}\ { m pH}=7-8$
Phenylhydroxylamine	purple	pH = 4-10 without oxygen reacts too
Nitrosobenzene	purple	pH = 4-10 without oxygen reacts too
A _{53lina}	1	1
10		*
0.5		/-



4

of oxygen dissolved in water which was obtained by the method described in the Experimental. The standard deviation for three measurements is less than 10%.

As a matter of course this method is not specific for oxygen, other oxidizing agents interfere in this determination.

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C02 (M) × 10

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TITRIMETRIC DETERMINATION OF THIOCARBONATE SULPHUR

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Estimation of thiocarbonate sulphur with hydroxymercurybenzoic acid and N-bromosuccinimide is discussed. O-Hydroxymercurybenzoic acid involves direct titration with aqueous, potassium thiocarbonate in the presence of 0.05 M sodium hydroxide using thiofluorescein or dithizone as an indicator. One sulphur atom of thiocarbonate attaches itself to two molecules of O-hydroxymercurybenzoic acid whereas the other two separate as carbon disulphide. However, in acidic medium, N-bromosuccinimide is found to oxidise one sulphur atom of thiocarbonate to elementary sulphur and the other two separating as carbon disulphide. Use of N-bromosuccinimide involves a direct titration with thiocarbonate using methyl red as an indicator.

The following molar relationships are established: 2 mole of 0-hydroxymercurybenzoic acid $\equiv 1$ mole of Cs_3^{2-} , 1 mole of N-bromosuccinimide $\equiv 1$ mole of CS_3^{2-} .

Potassium thiocarbonate (PTC) has been used as an alternative for gaseous hydrogen sulphide in qualitative [1] and quantitative [2, 3] analysis of metal ions. Separation of metal ions by the WEISZ ringoven technique [4] and thin layer chromatography [5] using PTC has been reported in the literature. Use of PTC as a masking agent and as an indicator in EDTA titrations [6] was communicated earlier. The precipitated metal products obtained with PTC have been studied thermogravimetrically [7] to ascertain their stoichiometric compositions thereby establishing the degree of purity of the metal thiocarbonates and sulphides.

The various analytical applications of PTC have justified the determination of thiocarbonate sulphur content of aqueous samples of this reagent. Indirect standardisation of concentrated aqueous solutions of PTC employing gravimetric [8] and titrimetric [9, 10] methods has been reported earlier. However, no suitable direct method has been described so far for the estimation of thiocarbonate sulphur.

In the present communication, direct estimation of thiocarbonate sulphur using O-hydroxymercurybenzoic acid N-bromosuccinimide is reported.

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O-Hydroxymercurybenzoic Acid Method

WRONSKI [11] has pioneered the use of O-hydroxymercurybenzoic acid for the titrimetric determination of sulphur-containing compounds but without any reference to determination of thiocarbonate sulphur. A direct titration of thiocarbonate with O-hydroxymercurybenzoic acid using thiofluorescein or dithizone as an indicator has been achieved.

Experimental

Reagents

O-Hydroxymercurybenzoic acid, 0.05 M. Dissolve 16.0355 g of O-hydroxymercurybenzoic acid anhydride (Merck, analytical reagent grade) in 100 mL 1 M sodium hydroxide and dilute to one litre.

Thiofluorescein indicator

0.02 per cent solution in 1 M ammonia.

Dithizone

Freshly prepared 0.1 per cent ethanolic solution.

Potassium thiocarbonate (1 M)

An aqueous solution was prepared as previously described [8] and different working solutions made by dilutions as required.

Procedure

To a sample containing about 75 mg of thiocarbonate sulphur (or 25 mg of hydrolysable sulphur) add 5 mL sodium hydroxide solution and dilute to 100 mL. Add 1 mL of thiofluorescein indicator solution and titrate the blue-coloured solution immediately with 0.05 M O-hydroxymercurybenzoic acid to a faint yellow end point. (Dithizone indicator gives a yellow colour changing to purple at the end point). Calculate the thiocarbonate sulphur content of the sample solution from the relation

 $1 \text{ mL of } 1 \text{ } M \text{ } 0\text{-HMB} \equiv 0.0932 \text{ g } \text{K}_2 \text{CS}_3 \equiv 0.01603 \text{ g S}$

Discussion

The reaction of potassium thiocarbonate with *O*-hydroxymercurybenzoic acid using thiofluorescein or dithizone as an indicator corresponds to the following reaction:



Thus, 2 O-HMB = $K_2CS_3 = S$. Sulphite, thiosulphate and thiocyanate do not interfere in the determination. Accurate results were obtained between 5 and 24 mg oxidisable sulphur (see Table I).

Table I

Results of the determination of sulphur in potassium thiocarbonate with O-hydroxymercurybenzoic acid using thiofluorescein and dithizone as indicators

Volume of 0.05 M, potassium thiocarbon- ate taken, mL	Thiocarbonate sulphur present, mg	Sulphur* found ^a , mg	Sulphur* found ^b , mg	
3.0	14.43	4.80	4.80	
5.0	24.04	8.01	8.00	
8.0	38.47	12.84	12.82	
10.0	48.08	16.04	16.03	
12.0	57.71	19.26	19.26	
15.0	72.12	24.04	24.06	

* Hydrolysable sulphur is one-third of the total sulphur.

^a Thiofluorescein used as an indicator

^b Dithizone used as an indicator

N-Bromosuccinimide Method

N-Bromosuccinimide [12] is an oxidising agent, often highly selective and can decolorise methyl red in an aqueous acidic medium. It oxidises thiocarbonate preferentially. The red colour of the indicator remains unchanged until all the thiocarbonate ions present have been oxidised. The slightest excess of *N*-bromosuccinimide added after all the thiocarbonate has been oxidised decolorises the methyl red.

Reagents

Methyl red solution, 0.04 per cent, m/V, in 95 per cent ethanol.

Buffer solution

Buffer solution of pH 5 (sodium acetate-hydrochloric acid) was used. Other pH value required were obtained by the addition of appropriate amounts of acid or alkali to the buffer.

N-Bromosuccinimide solution, 0.1 per cent (m/V)

Aqueous solution was prepared by dissolving analytical grade N-bromosuccinimide in deionized water. The solution was kept in a dark-glass bottle.

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Potassium thiocarbonate (1 M)

An aqueous solution was prepared as previously described [8] and different working solution made by dilution as required.

Procedure

To an accurately measured volume of potassium thiocarbonate (containing 5 to 10 mg) solution in a 100 mL conical flask add 20 mL of buffer solution and adjust the pH between 4 and 7. Cool the content of the conical flask by placing into ice for about 10 minutes. Add 2 drops of methyl red indicator solution and titrate the mixture with 0.1 per cent N-bromosuccinimide in 0.01 M hydrochloric acid, added dropwise from a microburette graduated at 0.01 mL intervals with continuous shaking. The end point is reached when the last drop of titrant discharges the red colour. Calculate the potassium thiocarbonate content from the expression:

Potassium thiocarbonate present, $mg = \frac{186.4 VC}{178}$ where V is the titre of N-bromo-

succinimide solution in mL and C is the amount of N-bromosuccinimide solution in mg per mL. 186.4 and 178 are the molecular masses of potassium thiocarbonate and N-bromosuccinimide, respectively.

Discussion

It is evident from the results shown in Table II that *N*-bromosuccinimide reacts quantitatively with potassium thiocarbonate in a 1:1 mole ratio as shown by the equation:

$$\begin{array}{c|ccccc} H_2C - CO \\ & N - B_1 & + & K_2CS_3 & + & z \ HCl \\ H_2C - CO \end{array}$$

$$\xrightarrow{H_2C-CO} NH + S + CS_z + HB_I + 2KCI$$

H₂C-CO

Thus, NBS \equiv K₂CS₂ \equiv S

N-bromosuccinimide in the presence of hydrochloric acid oxidises one of the three sulphur atoms present in thiocarbonate the other two sulphur atoms separating as carbon disulphide. The presence of carbon disulphide was confirmed by a colorimetric test [13]. A test for the presence of hydrobromic acid was made by adding chlorine water dropwise to 5 mL of the clear solution to which 2 mL of chloroform was added. The mixture was shaken, and the chloroform layer acquired a reddish brown colour after being allowed to stand. Solutions of potassium thiocarbonate of concentration up to 10 mg

Ta	b	le	п
			_

Potassium thiocar- bonate content, mg	Thiocarbonate sulphur present, mg	Titre of 0.1 per cent N-bromo- succinimide, mg	Sulphur found,* mg	
5.0	2.58	4.80	0.86	
6.0	3.10	5.71	1.03	
7.0	3.61	6.66	1.20	
8.0	4.13	7.60	1.37	
9.0	4.64	8.55	1.54	
10.0	5.16	9.51	1.71	

Results of the determination of sulphur in potassium thiocarbonate with N-bromosuccinimide as an oxidising titrant

* Oxidisable sulphur is one-third of the total sulphur.

give quantitative results whereas solutions of higher concentrations tend to loose hydrogen sulphide on acidification

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COMPLEXES OF SOME SEMICARBAZONES AND THIOSEMICARBAZONES WITH CHROMIUM(III)

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Chromium(III) complexes of type $\operatorname{CrL}_2X_3 \cdot nH_2O$ where L is semicarbazone, $\operatorname{NH}_2\operatorname{CONHN} : \operatorname{CR}_1R_2$ and thiosemicarbazone $\operatorname{NH}_2\operatorname{CSNHN} : \operatorname{CR}_1R_2$ ($\operatorname{R}_1R_2 = \operatorname{cyclopentane}$ or cycloheptane and X = Cl, Br, I or NO₃ and n = 0-2) have been prepared and characterized. Magnetic moments, electronic spectra and electron spin resonance spectra of the complexes have been discussed. All the complexes are high-spin sixcoordinate octahedral.

Introduction

Since DOMAGK's original discovery [1] of their antitubercular activity, thiosemicarbazones have been shown to be pharmacologically active against viruses protozoa, small pox and certain kinds of tumour [2]. The corresponding semicarbazones on the other hand appear to be inactive. In at least one case it has been shown that the active species is not the thiosemicarbazone itself but a metal chelate of the thiosemicarbazone [3].

This paper describes preparation and characterization of chromium(III) complexes, $CrL_2X_3 \cdot nH_2O$ where $L = semicarbazones H_2NCONHN : CR_1R_2$ or thiosemicarbazones $H_2NCSNHN : CR_1R_2$ (R_1 and $R_2 = cyclopentane$ and cycloheptane and X = Cl, Br, I or NO₃ and n = 0-2.

All the complexes are high-spin six-coordinate octahedral. The nitrato complexes show isomerism arising from monodentate and bidentate behaviour of the nitrato group. The nature of the metal-ligand band has been discussed on the basis of magnetic, spectral and esr data. Chromium(III) is a typical hard metal ion. Nitrogen, sulphur and oxygen donor ligands behave as soft or hard bases depending on the metal ion.

Experimental

Preparation of ligands

All ligands were prepared by the methods reported earlier [4a].

Preparation of complexes

All the complexes were prepared by a general method. Hot EtOH solution of the respective chromium salt (0.05 mole) was mixed with hot EtOH solution of the respective ligand (0.1 mole). The mixture was refluxed on a water bath for about four hours. After refluxing the mixture was concentrated upto half of its volume. On cooling the mixture overnight in a refrigerator, green to violet crystals separated out, which were filtered, washed with ethanol and dried in an electric oven.

All the complexes are soluble in water, ethanol and methanol but insoluble in benzene, chloroform and ether.

Physical measurements

Magnetic susceptibility measurements were carried out by the GOUY method using $Hg[Co(CNS)_4]$ ($\chi_g = 16.44 \times 10^{-6}$ cgs unit at 20 °C) as a calibrating agent. Electronic spectra

<u> </u>	Calaura	Element analysis; Found (Calcd.)					
Compound	Colour	% Cr	% C	% H	% N		
$Cr(cpsc)_2Cl_3$	Green	$12.36 \\ (12.40)$	32.50 (32.47)	4.90 (4.96)	18.90 (18.94)		
$Cr(cpsc)_2Br_3$	Green	9.45 (9.50)	24.80 (24.87)	3.85 (3.80)	14.60 (14.51)		
$Cr(cpsc)_2I_3$	Green	7.60 (7.66)	20.08 (20.05)	3.05 (3.06)	$11.70 \\ (11.70)$		
$Cr(cpsc)_2(NO_3)_3$	Violet	$10.30 \\ (10.32)$	27.58 (27.53)	4.25 (4.21)	24.05 (24.09)		
$Cr(cptsc)_2Cl_3$	Green	$ \begin{array}{r} 11.38 \\ (11.36) \end{array} $	30.25 (30.28)	4.68 (4.63)	17.65 (17.66)		
$Cr(cptsc)_2Br_3$	Green	8.80 (8.84)	23.58 (23.57)	3.62 (3.60)	13.78 (13.75)		
$Cr(cptsc)_2I_3$	Green	7.15 (7.20)	19.8 (19.2)	2.90 (2.93)	11.23 (11.2)		
$Cr(cptsc)_2(NO_3)_3$	Violet	9.75 (9.73)	25.98 (25.94)	3.90 (3.96)	22.76 (22.70)		
$Cr(chepsc)_2CJ_3 \cdot 1.5 H_2O$	Green	$10.15 \\ (10.16)$	36.70 (36.46)	5.98 (6.34)	15.81 (15.95)		
$Cr(chepsc)_2Br_3 \cdot 2 H_2O$	Green	8.05 (8.09)	28.82 (28.82)	4.52 (5.02)	12.61 (12.61)		
$Cr(chepsc)_2I_3 \cdot 2 H_2O$	Green	6.75 (6.79)	23.82 (23.70)	3.98 (4.19)	10.38 (10.37)		
$Cr(chepsc)_2(NO_3)_3 \cdot 2 H_2O$	Violet	8.90 (8.94)	31.40 (31.22)	4.88 (5.22)	20.60 (20.48)		
$Cr(chaptsc)_2Cl_3 \cdot 2 H_2O$	Green	9.55 (9.69)	34.08 (33.83)	5.33 (6.08)	14.92 (14.80)		
$Cr(chaptsc)_2Br_3 \cdot 2 H_2O$	Green	7.75 (7.87)	27.40 (27.50)	4.32 (4.47)	12.03 (12.03)		
$Cr(chaptsc)_2I_3 \cdot 2 H_2O$	Green	6.45 (6.53)	22.90 (22.80)	3.57 (4.04)	10.03 (9.97)		
$Cr(chaptsc)_2(NO_3)_3 \cdot 2 H_2O$	Violet	8.41 (8.50)	29.82 (29.67)	4.63 (5.20)	19.62 (19.47)		

 Table I

 Colour and composition of complexes

were recorded on Russian CØ-10 automatic recording and SP-600 manual spectrophotometers. I. R. spectra were recorded on Perkin-Elmer 137 and 621 models in KBr pellets. ESR spectra of powdered solid complexes were recorded on a Varian E_4 -EPR spectrometer operating at \sim 9.4 GHz and 100 KHz field modulation and phase sensitive detection.

Result and Discussion

Elemental analyses (Table I) reveal a general composition $\operatorname{CrL}_2X_3 \cdot n\operatorname{H}_2O$ (X = Cl, Br, I or NO₃ and n = 0-2) for complexes of all the ligands. With thiosemicarbazide tris chelate CrL_3X_3 has been reported [4b]. With our ligands, however, tris chelate could not be obtained even if the preparations were carried out using an excess of the ligand. Steric hindrance due to the bulky ligands may be a possible reason. Infrared spectra of these ligands [4a] and complexes indicate that ligands show bidentate behaviour coordinated through hydrazinic nitrogen and O/S atoms: thus six-coordinate structure may be proposed for all the complexes, with two coordination sites occupied by the respective anions.

Complex	μ_{eff}		$ {}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F) $ $ (\nu_{2}) $
Cr(cpsc) ₂ Cl ₃	3.77	15 400	21 200
$Cr(cpsc)_2Br_3$	3.77	15 600	21 200
$Cr(cpsc)_2I_3$	3.81	15 700	21 400
$Cr(cpsc)_2(NO_3)_3$	3.75	16 600	23 500
Cr(cptsc) ₂ Cl ₃	3.80	15 600	21 200
Cr(cptsc) ₂ Br ₃	3.77	15 800	21 500
$Cr(cptsc)_2I_3$	3.78	15 800	21 500
$Cr(cptsc)_2(NO_3)_3$	3.81	17 000	24 800
$Cr(chepsc)_2Cl_3 \cdot 1.5 H_2O$	3.82	15 100	20 800
$Cr(chepsc)_2Br_3 \cdot 2 H_2O$	3.79	15 200	20 800
$Cr(chepsc)_2I_3 \cdot 2 H_2O$	3.77	15 200	20 800
$Cr(chepsc)_2(NO_3)_3 \cdot 2 H_2O$	3.75	16 600	23 500
$Cr(cheptsc)_2Cl_3 \cdot 2 H_2O$	3.74	15 600	21 200
$Cr(cheptsc)Br_3 \cdot 2 H_2O$	3.79	15 700	21 300
$Cr(cheptsc)_2I_3 \cdot 2 H_2O$	3.76	15 700	21 300
$Cr(cheptsc)_2(NO_3)_3 \cdot 2 H_2O$	3.77	17 200	25 000

Table II							
Magnetic	moments	(BM) and	electronic	spectra	(cm^{-1})		

The chloro, bromo and iodo complexes

The complexes show magnetic moments (Table II) in the range of 3.74-3.90 BM corresponding to three unpaired electrons [5].

As stated earlier six-coordinate tetragonal structure $[CrL_2X_2]X$ may be proposed for the complexes with planar arrangement of the ligands and the *axial* position occupied by anions. Molar conductance 360-380 mole cm⁻² in aqueous solution at 30 °C indicates 1 : 3 electrolytes [6]. This suggests that all the coordinated anions are replaced by water molecules resulting the formation of the $[CrL_2(H_2O)_2]^{3+}$ cation.

In an octahedral ligands field, ${}^{4}F$ ground state of chromium(III) is split into ${}^{4}A_{2}$, ${}^{4}T_{1}$ and ${}^{4}T_{2}$ states. The only other ligand field states that have been observed in chromium(III) spectra are ${}^{4}T_{1}$ (${}^{4}P$) and ${}^{2}E$, ${}^{2}T_{1}$ and ${}^{2}T_{2}$ derived from ${}^{2}G$. A complete ligand field calculation has been made by LIEHR [7]. The three spin-allowed d-d transitions are the following [8]:

 ${}^{4}\!A_{2g}(F) \to {}^{4}\!T_{2g}(F), \ {}^{4}\!A_{2g}(F) \to {}^{4}\!T_{1g}(F) \quad \text{and} \quad {}^{4}\!A_{2g}(F) \to {}^{4}\!T_{1g}(P).$

The electronic spectra of the complexes recorded in nujol mull show bands at 15 400-16 000 and 21 000-25 000 cm⁻¹ (Table II). These two spin-allowed transitions may be assigned to the ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)(v_{1})$, and ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{1g}(F)(v_{2})$ transitions, respectively. The third spin-allowed ${}^{4}A_{2g}(F) \rightarrow$ $\rightarrow {}^{4}T_{1g}(F)$ transition expected to appear [9] above 30 000 cm⁻¹ is usually not observed due to charge-transfer bands in the ultraviolet region. In present studies, however, this region was not recorded.

The nitrato complexes

These complexes also show magnetic moments corresponding to three unpaired electrons (Table II).

For all the nitrato complexes, infrared bands are observed corresponding to both coordinated and uncoordinated nitrato group [10]. Infrared



Fig. 1. IR spectra of; (a) Cr(Chepsc)₂Cl₃, (b) Cr(chepsc)₂(NO₃)₃

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absorptions, assigned to coordinated nitrate occur at 1505-1475 (v_1) , 1325-1275 (v_4) , 1045-1020 (v_2) and 808-803 cm⁻¹ (v_6) [11-14].

The complexes under study show infrared bands (Fig. 1) at 1480-1490 (v_1) , 1390 (v_3) , 1290-1295 (v_4) , 1010-1020 (v_2) and 810-820 cm⁻¹ (v_6) . For a choice between the monodentate and bidentate behaviour of the nitrate group, it has been observed that the extent of splitting of v_3 is larger in the latter case, but this criterion has failed in a large number of complexes [10]. Broad absorption band at 1390 cm⁻¹ corresponds to the v_3 of uncoordinated nitrate group. It can not be decided whether the nitrate group acts as a monodentate or a bidentate ligand, *i.e.*, whether the complexes have the structure [CrL₂(NO₃)₂]NO₃ or [CrL₂(NO₃)](NO₃)₂. Conductance measurements are also of little help since the aqueous solution of all the complexes show conductance for tri-univalent electrolyte [6] (~400 mol cm⁻²) suggesting that all the coordinated anions are replaced by water molecules resulting in the formation of [CrL₂(H₂O)₂]³⁺ cations.

Electronic spectra (Figs 2 and 3) of the complexes also show two bands (Table II) corresponding to ${}^{4}A_{2g}(F) \rightarrow {}^{4}T_{2g}(F)$ (r_{1}) and ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}(F)$ (r_{2}) . It is important to note that chloro complexes are green and nitrato complexes are violet in colour. This difference in colour is associated with a marked difference in the electronic spectra as discussed below. It has also been observed that on standing the aqueous solution of nitrate complexes show a colour change for violet to green. It is indicated, therefore, that green coloured species is comparatively more stable and hence, has a *trans*-structure, the violet species thus being *cis*. Green coloured trans complexes and violet coloured *cis* complexes of chromium(III) with ammonia are also known [15].



Fig. 2. Visible spectra of; (a) $Cr(chtsc)_2Cl_3$, (b) $Cr(cptsc)_2(NO_3)_3$, (c) $Cr(cpsc)_2Cl_3$, (d) $Cr(cpsc)_2(NO_3)_3$



Fig. 3. Visible spectra of; (a) $Cr(cheptsc)_2Cl_3$, (b) $Cr(cheptsc)_2(NO_3)_3$, (c) $Cr(chepsc)_2Cl_3$, (d) $Cr(chepsc)_2(NO_3)_3$

For the same ligand the nitrato complexes show stronger ligand field then the corresponding chloro, bromo and iodo complexes. The extent of spectral shift from halo to nitrato complex is of the order of approximately 2000 cm⁻¹ which by no means may be attributed to the difference in the ligand field strengths of the two anions. Rather it may be attributed to the *cis*- and *trans*-structure of the complexes, *cis*-and *trans*- $[Co(NH_2NHCSNH_2)_3]^{3+}$ are known [16] to give rise 10 Dq values of 19 400 and 18 200 cm⁻¹, respectively. The *cis*-configuration in the nitrato complexes, as against the *trans*-configuration in the halo complexes, appears to have been imposed by a bidentate nitrato group occupying two *cise*positions. From the 10 Dq values obtained for CrL_2X_3 (X = Cl, Br, or I) and $Cr(L)_2(NO_3)_3$, applying the rules of average environments, two different values of Dq may be obtained for the hypothetical anions $[Cr(L)_3]^{3+}$ corresponding to *cis*- and *trans*-arrangements of the ligand in a tris chelates.

The ligand field parameters

The energy of the first spin-allowed transition ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$ directly gives the values of 10 Dq. The thiosemicarbazone complex has higher Dq values compared to the corresponding semicarbazone complex. This is in line with the higher position of sulphur atom as donor compared to the oxygen atom in the spectrochemical series [17]. Thiosemicarbazide complexes are also known

to have larger Dq values compared to the corresponding semicarbazide complexes [18].

$$B = \frac{2\nu_1^2 - 3\nu_1\nu_2 + \nu_2^2}{15\nu_2 - 27\nu_1}$$

where v_1 and v_2 are the energies of the first and second spin-allowed transitions, respectively. The nephelauxetic ratio parameter β is readily obtained using the relation $\beta = B(\text{complex})/B(\text{free ion})$ where B free ion = 0.918 kK. The results are tabulated in Table III. The values of β are such similar to that of earlier reported N-S bonded and N-O bonded donor ligands [19]. This value of β indicates less covalent character of the metal ligand σ -bond. According to JORGENSEN [20] for a 3d transition metal with cationic charge Z and the occupation number of the Dq shell q, the RACAH interelectronic repulsion parameters, B can be expressed by the relation; $B(\text{cm}^{-1}) = 384 + 58 q +$ + 124 (Z + 1) - 540/(Z + 1). From this relation the values of Z for the present complexes lie in the range of 1.02-1.39 (Table III) which is considerably below than the formal +3 oxidation state of chromium. Some other ligand field parameters viz., Dt, Dq^{xy} and Dq^z have also been evaluated and these have been used to calculate NSH parameters viz., DT, DQ, DQ^{xy}, Dq^z and degree of distortion in terms of (DT/DQ) (Table IV).

The transition v_2 is equal to $10 Dq^{xy}$ and the separation between v_1 and v_2 is equal to the first order, (35/4)Dt and Dt is related to the in-plane field strengths as $Dt = (4/7) (Dq^{xy} - Dq^2)$, where Dq^{xy} and Dq^2 are in-plane (xy) and out-of-plane (z) field strengths, respectively. The values of these parameters are comparable to those observed for other chromium [21] complexes involving similar set of chromophores. However, it may be pointed out that these parameters are not standardised and this require modifications. To overcome the shortcomings of various parameters of classical Hamiltonian for the tetragonal complexes, LEVER *et al.* [22, 23] have recently advanced the theory of Normalised Spherical Harmonic (NSH) Hamiltonian. The NSH parameter DQ, DS, DT, DQ^{xy} and DQ^2 are fully capitalized to relate them to the corresponding crystal field parameters, yet emphasize their distinction. The parameters are calculated as [23]:

DS = -7Ds (not possible in present state)

$$egin{aligned} DT &= \left(rac{7\sqrt[3]{(15)}}{2}
ight) Dt \ DQ &= \left(6\sqrt{(21)} \ Dq^{xy}
ight) - \left(rac{7\sqrt[3]{21}}{2}
ight) DT \,. \end{aligned}$$

The NSH parameters are more useful, (a) the theory takes into account on off-diagonal contribution to Dt, (b) DQ is a measure of the average ligand

Complex	$10 Dq m cm^{-1}$	B cm ⁻¹	β	λ	λ*	g	Z	λ**	L.F.S.E. Kcal/mole
Cr(cpsc) ₉ Cl ₃	15 400	569	.62	47.77	.52	1.978	1.07	.62	52.80
Cr(cpsc) ₉ Br ₃	15 600	542	.59	51.28	.57	1.976	1.02	.59	53.48
Cr(cpsc) ₂ I ₂	15 700	554	.60	47.50	.64	1.973	1.04	.60	53.83
$Cr(cpsc)_{2}(NO_{2})_{2}$	16 600	699	.76	42.12	.47	1.982	1.39	.76	56.91
Cr(cptsc) ₂ Cl ₂	15 600	542	.59	59.08	.66	1.972	1.02	.59	53.83
$C_{D}(cptsc)_{2}Br_{2}$	15 800	553	.60	53.92	.60	1.975	1.04	.60	54.17
Cr(cptsc) ₂ I ₂	15 800	553	.60	44.04	.49	1.980	1.04	.60	54.17
$Cr(cptsc)_2^{-3}$	17 000	680	.74	43.13	.48	1.892	1.28	.74	58.28
$Cr(chepsc)_{\circ}Cl_{\circ} \cdot 1.5 H_{\circ}O$	15 200	559	.61	43.97	.49	1.979	1.05	.61	51.77
$Cr(chepsc)_2 Br_2 \cdot 2 H_2 O$	15 200	546	.59	38.57	.43	1.982	1.03	.59	52.11
$Cr(chepsc)_{a}I_{a} \cdot 2 H_{a}O$	15 200	546	.59	40.47	.45	1.981	1.03	.59	52.11
$Cr(chepsc)_2 = 3 = 2 = 2$	16 600	699	.76	48.34	.53	1.979	1.39	.76	56.91
$Cr(cheptsc)_2(1 + 2 + 3)_3 = -2$	15 600	542	.59	47.38	.53	1.978	1.02	.59	53.48
$Cr(cheptsc)_2 Br_0 \cdot 2 H_0 O$	15 700	542	.59	43.76	.49	1.980	1.02	.59	53.83
$Cr(cheptsc)_2 = 3$ = -2^{-1}	15 700	542	.59	43.76	.49	1.980	1.02	.59	53.83
$Cr(cheptsc)_2(NO_3)_3 \cdot 2 H_2O$	17 200	820	.89	43.64	.48	1.982	1.39	.89	58.97

 Table III

 Ligand field parameters
Compound	$10 Dq^{xy}$	$10 Dq^{z}$	Dı	DQ	DQ^{xy}	DQ^x	DT	DT/DQ
Cr(cpsc) ₂ Cl ₃	21 200	960	663	85 873	96 510	64 599	8 987	.1046
Cr(cpsc) ₂ Br ₃	21 200	1000	640	80 868	91 134	60 336	8 675	.1072
$Cr(cpsc)_2I_3$	21 400	1001	651	82 708	93 151	61 822	8 824	.1066
$Cr(cpsc)_2(NO_3)_3$	23 500	971	788	106 720	119 362	81 436	10 681	.1000
Cr(cptsc) ₂ Cl ₃	21 200	975	640	80 868	91 134	60 336	8 675	.1072
Cr(cptsc) ₂ Br ₃	21 500	861	651	82 434	92 876	61 550	8 824	.1070
Cr(cptsc) ₂ I ₃	21 500	861	651	80 043	90 309	59 511	8 675	.1083
Cr(cptsc) ₂ (NO ₃) ₃	24 800	921	891	125 540	139 832	96 956	10 277	.0962
Cr(chepsc) ₂ Cl ₃ · 1.6 H ₂ O	20 800	941	651	80 868	913 130	56 302	8 824	.1091
$Cr(chepsc)_2Br_3 \cdot 2 H_2O$	20 800	935	640	84 358	94 624	63 826	8 675	.1028
$Cr(chepsc)_2I_3 \cdot 2 H_2$	20 800	935	640	81 968	92 234	61 436	8 675	.1058
$(chepsc)_2(NO_3)_3 \cdot 2 H_2O$	24 500	971	788	106 722	119 362	81 436	10 681	.1000
$Cr(cheptsc)_2Cl_3 \cdot 2 H_2O$	21 200	1000	640	80 868	91 134	60 336	8 675	.1072
$ m Cr(cheptsc)_2Br_3 \cdot 2 H_2O$	21 300	1010	640	80 593	90 859	60 061	8 675	.1076
$Cr(cheptsc)_2I_3 \cdot 2 H_2O$	21 300	1010	640	80 593	90 859	60 061	8 675	.1076
$Cr(cheptsc)_2(NO_3)_3 \cdot 2 H_2O$	25 000	941	891	124 963	139 255	96 379	$12\ 077$.0966

Table	IV

NSH parameters

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CHANDRA: COMPLEXES OF SEMICARBAZONES

field experimented by metal ion, unlike the classical Dq which is the measure of in-plane field only and (c) the parameters of NSH theory are independent of the coordinate system used for calculations and may be compared with the crystal field of angular overlap parameters to determine restrictions of these values. The parameters DQ^{xy} (in-plane field strength) and DQ^z (out-ofplane) field strength are determined by the equations:

$$egin{aligned} DQ &= \left(rac{1}{\sqrt{6}}
ight) \left(4 \ DQ^{xy} + 2 \ DQ^{z}
ight) \ DT &= \left(rac{\sqrt{5}}{\sqrt{7}}
ight) \left(DQ^{xy} - DQ
ight) \end{aligned}$$

However, it may be pointed out that these parameters have artificial significance for DQ itself is a measure of average ligand field strength.

Further, the relation of (DT/DQ) has been shown to be a measure of the degree of tetragonal distortion. The values of (DT/DQ) for these complexes (Table IV) lie in the range .0962-.1091. These values are much lower than the limiting value (0.4226) for square planar complexes and suggest a small distortion from idealised cubic symmetry.

ESR spectra of the powdered samples of chromium(III) complexes consist in each case of a single broad line with peak to peak separation of about 220G. The g-values are listed in Table III. In the crystal field theory, 'he values of g is given by the equation,

$$g = 2.0023 - \frac{8\lambda}{\varDelta E(T_{2g})}$$

where λ is the effective spin-orbit coupling constant for the metal ion in the complex. OWEN [24] noted that the reduction of spin-orbit coupling constant from the free ion value of 90 cm⁻¹ for chromium(III) can be employed as a measure of metal-ligand covalency. It is possible to define covalency parameters, analogous to nephelauxetic parameters which is the ratio of the spin-orbit coupling constant for the complex and for free Cr³⁺ ion.

CORE and GARRET [25] have obtained the following relation, $\lambda = 0.0110$ $(B + 1.080)^3 + 0.0062$, connecting the RACAH interelectronic repulsion parameter B (in kK) to λ (in kK) for chromium(III) complexes. The value of λ are listed in Table III. It is observed that the λ values evaluated using the empirical relation are consistently lower than those obtained from esr data. The real value of empirical relation of λ and B is in its ability to allow reasonable estimates of λ or B if either can be determined experimentally.

It is very interesting to note that in these complexes the semicarbazones and thiosemicarbazone complexes show similar nephelauxetic effects. Further

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in the halo and nitrato complexes of the same ligand having, respectively, trans- and cis-arrangement, there is considerable difference in the metalligand covalency.

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CAFFEINE ADDUCTS OF COPPER(II) HALOGENOPROPIONATES

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Light-green copper(II) and halogenopropionates with caffeine were synthetized and characterized by elemental analysis, as well as by infrared spectroscopy and EPR method. Magnetic measurements were determined in the temperature range of 81 -300 K. The data were compared with those reported for binuclear copper(II) carboxylates. The correlation between the magnetic and spectroscopic data as well as the acidity of the appropriate acids were discussed.

Introduction

Approximately planar structure of caffeine hydrochloride has been X-ray established by MERCER and TROTTER [1]. Few copper(II) compounds with caffeine were subjected to investigation and caffeine was found to coordinate as a monodentate ligand through the imidazole nitrogen atom [2-6]. Copper(II) halogenopropionates with caffeine as a ligand have not been studied yet and that was the purpose to our work.

The compound of the general formula CuX_2caf (where $X = BrCH_2CH_2COO^-$, $CH_3CHBrCOO^-$, $BrCH_2CHBrCOO^-$, $CH_3CHClCOO^-$ or $CH_3CCl_2COO^-$; caf = caffeine) was synthetized to examine the donor properties of caffeine.

The magnetic and spectroscopic investigations of CuX_2 caf compounds are the continuation of our studies on the properties of copper dimers [7-9].

Experimental

Synthesis

Copper(II) halogenopropionates of the general formula CuX_2caf (X = BrCH₂CH₂COO⁻, CH₃CHBrCOO⁻, CH₃CHClCOO⁻, BrCH₂CHBrCOO⁻, BrCH₂CHBrCOO⁻ or CH₃CCl₂COO⁻) were prepared by adding an excess of caffeine and a small amount of the appropriate free acid to a hot methanol solution of CuX_2 . The reaction mixture was heated, stirred and allowed to stand at room temperature. Under the evaporation of the solvent green powder was obtained. Recrystallization from methanol yielded light-green microcrystals. Analytical data are given in Table I.

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	1		,		
Compound		Cu %	С %	Н %	N %
Cu (CH₃CH ClCOO) ₂ caf	Calcd. Found	$13.44\\13.42$	$\begin{array}{c} 35.56\\ 35.00 \end{array}$	$\begin{array}{c} 3.84\\ 3.76\end{array}$	$11.85 \\ 11.88$
$Cu(CH_3CCl_2COO)_2caf$	Calcd. Found	$11.73 \\ 11.88$	$\begin{array}{c} 31.04 \\ 31.00 \end{array}$	2.98 3.10	$\begin{array}{c} 10.34 \\ 10.29 \end{array}$
$Cu(BrCH_2CH_2COO)_2caf$	Calcd. Found.	$\begin{array}{c} 11.31\\ 11.33\end{array}$	$\begin{array}{c} 29.94\\ 29.60\end{array}$	$\begin{array}{c} 3.23\\ 3.16\end{array}$	9.97 9.95
Cu(CH ₃ CHBrCOO) ₂ caf	Calcd. Found	$\begin{array}{c} 11.31\\ 11.22 \end{array}$	$\begin{array}{c} 29.94 \\ 29.30 \end{array}$	$\begin{array}{c} 3.23\\ 3.2 \end{array}$	9.97 9.81
Cu(BrCH ₂ CHBrCOO) ₂ caf	Calcd. Found	8.83 9.00	$\begin{array}{c} 23.37\\ 24.00\end{array}$	$\begin{array}{c} 2.24\\ 2.41\end{array}$	7.79 8.02

Table I

Analytical data

Spectroscopic studies

Electronic spectra in the 1.0-3.0 μ m⁻¹ region were taken on a Perkin-Elmer 450 spectrophotometer and infrared spectra in the region 400-4000 cm⁻¹ with a Perkin-Elmer 225 spectrophotometer.

In both cases the nujol suspension technique was used. Electron paramagnetic resonance spectra of the polycrystalline samples were taken on a JES-3MX spectrometer at room temperature.

Magnetic susceptibility measurements

Magnetic susceptibility measurements have been made in the range of 81-300 K by the Gouy method. Mercury tetrathiocyanatocobaltate(II) was used as a calibrant [10].

The molar susceptibilities were corrected for diamagnetism using Pascal constants [11] and for T.I.P. equal $60 \cdot 10^{-6}$ cm³ mol⁻¹ per Cu atom. The effective magnetic moments were calculated from the expression: $\mu_{\text{eff}} = 2.83 \ (\chi_{\text{M}} T)^{1/2}$.

Table II

Spectroscopic data

ν _{as} (COO [−]) (cm ^{−1})	$\nu_{8}(COO^{-})$ (cm ⁻¹)	Band I (µm ⁻¹)	Band II ^a (µm ⁻¹)	pKab
1665, 1625	1415	1.40	2.70 sh	4.06
1660, 1640	1420	1.39	2.70 sh	3.01
1665, 1640 sh	1415	1.39	2.70 sh	2.879
1650, 1630 sh	1410	1.36	2.70 sh	≈2
1670, 1640 sh	1400	1.33	2.70 sh	~1.5
	$\begin{array}{c} \nu_{as} ({\rm COO}^{-}) \\ ({\rm cm}^{-1}) \end{array}$ 1665, 1625 1660, 1640 1665, 1640 sh 1650, 1630 sh 1670, 1640 sh	$\begin{array}{ c c c c c } \hline \nu_{as}(COO^{-}) & \nu_{s}(COO^{-}) & (cm^{-1}) \\ \hline 1665, 1625 & 1415 \\ 1660, 1640 & 1420 \\ 1665, 1640 & sh & 1415 \\ 1650, 1630 & sh & 1410 \\ 1670, 1640 & sh & 1400 \\ \hline \end{array}$	$\begin{array}{ c c c c c } \hline \nu_{as}(COO^{-}) & (cm^{-1}) & (cm^{-1}) & (cm^{-1}) & (\mu m^{-1}) \\ \hline 1665, 1625 & 1415 & 1.40 \\ 1660, 1640 & 1420 & 1.39 \\ 1665, 1640 & sh & 1415 & 1.39 \\ 1650, 1630 & sh & 1410 & 1.36 \\ 1670, 1640 & sh & 1400 & 1.33 \\ \hline \end{array}$	$\begin{array}{ c c c c c c } \hline \nu_{as}(COO^{-}) & (cm^{-1}) & (cm^{-1}) & (cm^{-1}) & Band I \\ \hline \mu m^{-1} & (\mu m^{-1}) & (\mu m^{-1}) & (\mu m^{-1}) \\ \hline 1665, 1625 & 1415 & 1.40 & 2.70 \text{ sh} \\ 1660, 1640 & 1420 & 1.39 & 2.70 \text{ sh} \\ 1665, 1640 \text{ sh} & 1415 & 1.39 & 2.70 \text{ sh} \\ 1650, 1630 \text{ sh} & 1410 & 1.36 & 2.70 \text{ sh} \\ 1670, 1640 \text{ sh} & 1400 & 1.33 & 2.70 \text{ sh} \\ \hline \end{array}$

^a sh = shoulder, ^b pKa - values of the respective acid

Results and Discussion

The infrared spectrum of CuX_2 caf compounds shows strong absorption bands near 1400 and 1650 cm⁻¹ assigned to the symmetric and antisymmetric vibrations of the carboxylate group (COO⁻). The band positions (Table II) are characteristic for copper(II) carboxylates [12] and indicative for coordination of both oxygen atoms of the carboxyl group to the copper atoms [13]. The absorption band at \sim 1230 cm⁻¹ has been assigned to the -C-N=Cstretching vibration of the coordinated caffeine, because this band is downfield shifted compared with the corresponding band of the free caffeine [6]. This indicates that coordination of caffeine to copper(II) proceeds through the imidazole nitrogen atom.

The bands of electronic spectra are given in Table II. The band positions are comparable to those reported for binuclear copper(II) carboxylates [14]. Band I in the red region of the spectrum is sensitive to the nature of the anion. The systematic shift of Band I with simultaneous decrease of the pKa value of the appropriate acid was observed. This is in agreement with the expected decrease in ligand field. Similar correlation has been found in the case of copper(II) propionates with antipyrine [15] and copper(II) chloroacetates [16, 17].

Electron paramagnetic resonance spectra taken at room temperature showed peaks characteristic for *axially* symmetric binuclear species. The EPR parameters are listed in Table III.

The compounds show subnormal magnetic moments at room temperature (Table IV), exhibit temperature dependent susceptibility characteristic to molecular antiferromagnetism (Fig. 1).

ET R parameters							
Compound	g_ /	g ¹¹	gav	D (cm ⁻¹)			
Cu(BrCH ₂ CH ₂ COO) ₂ caf	2.087	2.345	2.176	0.349			
Cu(CH ₃ CHBrCOO) ₂ caf	2.099	2.360	2.189	0.359			
Cu(CH ₃ CHClCOO) ₂ caf	2.104	2.372	2.197	0.367			
Cu(BrCH ₂ CHBrCOO) ₂ caf	2.099	2.387	2.199	0.369			
Cu(CH ₃ CCl ₂ COO) ₂ caf	2.098	2.403	2.204	0.382			

Table III

EPR parameters

Magnetic susceptibility data were fit to the equation:

$$\chi_{M} = \left\{ rac{N g_{am{x}}^{2} eta^{2}}{3kT} \left[1 - 1/3 (\mathrm{e}^{-2J/kT})
ight]^{-1}
ight\} (1 - m{x}) + \left(rac{N g_{lmp}^{2} eta^{2}}{4kT}
ight) m{x}$$

Compound	Т(К)	${\mathcal X}_{M} \cdot 10^{6} \ ({ m cm}^3 { m mol}^{-1})$	μ_{eff} (B.M.)	^a $K_{\rm eq}$				
Cu(BrCH ₂ CH ₂ COO) ₂ caf	293	740	1.32	0.582				
Cu(CH ₃ CHBrCOO) ₂ caf	291	743	1.32	0.563				
Cu(CH ₃ CHClCOO) ₂ caf	299	815	1.40	0.752				
Cu(BrCH ₂ CHBrCOO) ₂ caf	293	928	1.47	0.821				
$Cu(CH_3CCl_2COO)_2caf$	294	1014	1.54	0.953				

Table IV

Magnetic data

^a $K_{eq} = ext{singlet} \rightleftharpoons ext{triplet}$ equilibrium constant

where χ_M is molar magnetic susceptibility corrected for diamagnetism and t.i.p., x is the mole fraction of the mononuclear impurity; the other symbols have their usual meaning [18]. We have selected the apparent g_{av} values from the EPR spectra. All least squares fittings were computed on an Odra 1305 computer, using the BGD-1 programme.

The minimization of the sum of the squares of the deviation ERR =



Fig. 1. Temperature dependence of the molar magnetic susceptibility of the complexes: Cu(CH₃CHBrCOO)₂caf (1); Cu(BrCH₂CH₂COO)₂caf (2); Cu(CH₃CCl₂COO)₂caf (3); Cu(CH₃CHClCOO)₂caf (4); Cu(BrCH₂CHBrCOO)₂caf (5)

 $= \sum_{i} (\chi_{i}^{\text{calcd}} - \chi_{i}^{\text{exptl}})^{2} \text{ was used as the criterion to determine the best fit param$ $eters (Table V).}$

Table V

Exchange parameters and values of thermodynamic functions^a

-2J (cm ⁻¹)	Error ^b ERR · 10 ⁸	$\Delta H^{\circ} \ ({ m cm}^{-1}) \ (\pm 10)$	⊿S° (e.u.) (±0.2)
360	2.234	405	2.8
332	3.357	293	2.0
334	1.079	283	2.3
302	1.525	278	2.3
280	8.137	293	2.9
	2J (cm ⁻¹) 360 332 334 302 280	$\begin{array}{ c c c c }\hline & -2J & Error^b \\ \hline & (cm^{-1}) & ERR \cdot 10^8 \\ \hline & 360 & 2.234 \\ \hline & 332 & 3.357 \\ \hline & 334 & 1.079 \\ \hline & 302 & 1.525 \\ \hline & 280 & 8.137 \\ \hline \end{array}$	$\begin{tabular}{ c c c c c } \hline -2J & Error^b & dH^o \\ (cm^{-1}) & ERR \cdot 10^s & (cm^{-1}) \\ \hline & 360 & 2.234 & 405 \\ \hline & 332 & 3.357 & 293 \\ \hline & 334 & 1.079 & 283 \\ \hline & 302 & 1.525 & 278 \\ \hline & 280 & 8.137 & 293 \\ \hline \end{tabular}$

^a The mole fraction of the mononuclear impurity for all dimers equals zero ^b The sum of the squares of the residuals

The mole fractions of the singlet and triplet states were calculated from the observed susceptibilities by the method of HATFIELD et al. [19].

The singlet \rightleftharpoons triplet equilibrium constants obtained from the mole fractions were used for the calculations ΔH° and ΔS° .

The results are listed in Table V. The calculated enthalpy values are in a good agreement with the value of -2J. The entropy change values are close to 2.2 e.u. expected for the singlet \rightleftharpoons triplet equilibrium. The singlet-triplet splitting values -2J (Table V) decrease with an increase in acidity. Increase of acidity leads to a decrease of the electron density of the oxygen atom, followed by weakening of the metal-oxygen bond and by decreased overlap of orbitals of two unpaired electrons in the binuclear units. The zero field splitting parameter value, (D), increases with the acidity increase of the appropriate acids (Table III).

This parameter includes contributions from both exchange and dipoledipole interactions; these effects are opposite in charge. Increase of the -2Jvalue is accompanied with a decrease of the D parameter. The lowest D value was obtained in the case of Cu(BrCH₂CH₂COO)₂caf, in spite of the highest contribution of the dipole-dipole interaction. On the other hand, the highest D value in the case of Cu(CH₃CCl₂COO)₂caf, in spite of the lowest -2J value, indicates smallest contribution from the dipole-dipole interaction and therefore smallest reduction of the exchange interaction.

Similar correlation was found in the case of copper(II) propionates with 1,4-dioxane [20] and antipyrine [21]. It follows from Table VI, the -2J value for copper(II) halogenopropionates increases in the same order as the anions $CH_3CCl_2COO^- < BrCH_2CHBrCOO^- < CH_3CHClCOO^- < CH_3CHBrCOO^- < BrCH_2CHBrCOO^- < CH_3CHClCOO^- < CH_3CHBrCOO^- < content of the same order as the terminal ligands: anhydrous < dioxane < caffeine.$

Table VI

Compound	-2 J (cm ⁻¹)	pKa	Ref.
$\mathrm{Cu}(\mathbf{BrCH_2CH_2COO})_2 \ 0.5 \ \mathrm{C_4H_8O_2}$	325	4.06	[22]
Cu(BrCH ₂ CH ₂ COO) ₂ caf	360	4.06	this work
Cu(CH ₃ CHBrCOO) ₂	293	3.01	[22]
$Cu(CH_3CHBrCOO)_2 0.5 C_4H_8O_2$	304	3.01	[22]
Cu(CH ₃ CHBrCOO) ₂ caf	332	3.01	this work
Cu(CH ₃ CHClCOO) ₂	302	2.879	[22]
$Cu(CH_3CHClCOO)_2 0.5 C_4H_8O_2$	326	2.879	[22]
Cu(CH ₃ CHClCOO) ₂ caf	334	2.879	this work
Cu(BrCH ₂ CHBrCOO) ₂	286	≈ 2	[22]
$Cu(BrCH_2BrCOO)_2C_4H_8O_2$	292	≈ 2	[22]
Cu(BrCH ₂ CHBrCOO) ₂ caf	302	≈ 2	this work
Cu(CH ₃ CClCOO ₂)	252	≈ 1.5	[23]
$Cu(CH_3CCl_2COO)_2 0.5 C_4H_8O_2$	267	≈ 1.5	[23]
Cu(CH ₃ CCl ₂ COO) ₂ caf	280	≈ 1.5	this work

The values of -2J, for some copper(II) halogenopropionates compounds and pKa values of the respective acids

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RITTER-REAKTIONEN AN STEROIDEN, II*

REAKTION DER EPIMEREN 14,15-EPOXIDE UND DES 15β , 16β -EPOXIDS DER ÖSTRATRIEN-REIHE MIT ACETONITRIL UND BF₃-ETHERAT

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Die Ritter-Reaktion der epimeren 14,15-Epoxide ergibt vorwiegend unter Isomerisierung 15-Keto-Verbindungen. Daneben werden aus dem 14 α ,15 α -Epoxid 1 6% 14 β -Acetamino-15 α -alkohol 6 und aus dem 14 β ,15 β -Epoxid 10 15% 15 α -Acetamino-14 β -alkohol 13a isoliert. Unter den Bedingungen der Ritter-Reaktion erfolgt leicht eine Isomerisierung des 15 β ,16 β -Epoxids 14, so daß praktisch kein 16 α -Acetamino-15 β -alkohol 13a gewonnen werden kann. Ein präparativ gangbarer Weg (50–60%Ausbeute) zur Darstellung der Acetaminoalkohole führt über die aus den Epoxiden gut zugänglichen Azidoalkohole, die nachfolgend reduziert und acyliert werden. Die ¹H-NMR-Spektren und Massenspektren der Acetaminoalkohole werden diskutiert.

In Fortführung der Arbeiten über die Ritter-Reaktion von D-Ring-Epoxiden des Östratriens [1] untersuchten wir die epimeren 14,15-Epoxide 1 und 10 [2] sowie das 15β , 16β -Epoxid 14. Dabei interessierte, ob auf diese Weise weitere *trans*-Acetaminoalkohole der Östratrien-Reihe dargestellt werden können.

Von verschiedenen herzaktiven Steroiden mit einer 14,15-Epoxygruppe ist bekannt, daß unabhängig von deren Konfiguration der Angriff durch starke Nucleophile vorwiegend in der 15-Position und von der entgegengesetzten Seite unter Ausbildung *trans-diaxialer* Produkte erfolgt. Aus den 14 α ,15 α -Epoxiden werden dabei 15 β -substituierte 14 α -Hydroxyverbindungen und aus den 14 β ,15 β -Epoxiden 15 α -substituierte 14 β -Hydroxyverbindungen gebildet [3]. Durch schwächere Nucleophile werden 14,15-Epoxide hingegen zu 15-Ketoverbindungen isomerisiert [4]. Wir versuchten durch Ritter-Reaktion des 14 α ,15 α -Epoxids 1 15 β -Acetamino-14 α -hydroxy-östratriene zu erhalten.

Bei der Umsetzung des 14α , 15α -Epoxids 1 mit Acetonitril und BF₃-Etherat bei 0 °C entsteht nach 20 Minuten ein Gemisch, in dem kein Ausgangsprodukt mehr nachgewiesen werden kann. Das nach Aufarbeitung anfallende Rohprodukt wurde aus Methanol umkristallisiert. Dabei ließen sich 53% des 14β -konfigurierten 15-Ketons 2 abtrennen. Mit Hilfe der Schnellchromatographie an neutralem Aluminiumoxid (s. Experimenteller Teil) erfolgt die weitere Auftrennung der Mitterlauge, wobei 21% des 16,17-ungesättigten

* I. Mitteilung vgl. [1].

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Ketons 3 (entstanden durch Eliminierung von Essigsäure aus 2 bei Chromatographie), 3% des 8(9)-ungesättigten 15a-Alkohols 4, 5% des 14β,15a-Diols 5 und 6% der vicinalen trans-14 β -Acetamino-15 α -hydroxy-Verbindung 6 isoliert werden. Die Produktausbeute zeigt, daß die Isomerisierung des Epoxids 1 unter den sauren Bedingungen schneller abläuft, als der nucleophile Angriff des Acetonitrils. Bei Umsetzung des Epoxids 1 in Methylenchlorid mit BF3-Etherat ohne Nucleophil kann bereits nach 5 Minuten im Dünnschichtchromatogramm kein Ausgangsmaterial mehr nachgewiesen werden. Aus dem Rohprodukt ließen sich mit Hilfe der präparativen Schichtchromatographie 54% des 14 β -konfigurierten 15-Ketons 2, 8% des ungesättigten Ketons 3 und 21% der 15 α -Verbindung 4 gewinnen. Die 14 β -Konfiguration von 2 folgt aus der chemischen Verschiebung der 13-Methylprotonen $\delta = 1,17$ ppm (die Lage des 13-Methylsignals der bekannten 14-konfigurierten Verbindung 11 [5] wird bei $\delta = 0.91$ ppm gefunden) und der Kopplungskonstanten für das 17-Proton (J = 6 Hz) [6]. Die Ketogruppe (im IR-Spektrum durch die Acetatgruppe überdeckt) wird indirekt nach Reduktion mit NaBH4 in Methanol nachgewiesen. In Analogie zur Reduktion von 15-Oxo-cardenoliden [7] wurden 72% 17β -Acetoxy-3-methoxy- 14β -östra-1,3,5(10)-trien- 15α -ol 7 und 14% 17β -Acetoxy-3-methoxy-14 β -östra-1,3,5(10)-trien-15 β -ol 8 isoliert.

Aus 2 entsteht bei der Chromatographie an Aluminiumoxid oder unter Bedingungen der alkalischen Esterverseifung (K_2CO_3 /Methanol) unter Eliminierung von Essigsäure das 16,17-ungesättigte Keton 3, dessen Struktur durch die Tieffeldverschiebung des 13-Methylsignals bei 1,26 ppm und die beiden Dubletts der Vinylprotonen bei 6,02 und 7,53 ppm im ¹H-NMR-Spektrum sowie durch die erniedrigte Carbonylfrequenz bei 1695 cm⁻¹ im IR-Spektrum charakterisiert ist.

Die Zuordnung von 4 erfolgt in Anlehnung an KAMANO und Mitarbeiter [4], die 14 α ,15 α -Epoxide von Bufadienoliden mit Lewis-Säuren umsetzten. Im Massenspektrum findet man für 4 den gleichen Molpeak wie für das Ausgangsmaterial 1. Im IR-Spektrum wird eine Hydroxylbande bei 3627 cm⁻² beobachtet. Das UV-Spektrum weist ein für konjugierte Östratetraene typisches Maximum bei 274 nm auf [8]. Da im ¹H-NMR-Spektrum keine olefinischen Protonen gefunden werden, sollte die Doppelbindung zwischen den C-Atomen 8 und 9 liegen, zumal die Aromatenprotonen (H-2 und H-4) durch die Doppelbindung eine Tieffeldverschiebung erleiden. Aus der Kopplungskonstante für das 17-Proton ($\Sigma J = 11$ Hz) folgt bei bekannter 17 β -Konfiguration der Acetatgruppe eine 14 β -Konfiguration. Das Sextett des 15-Protons ($\Sigma J = 16$ Hz) erlaubt eine Zuordnung zum 15 α -konfigurierten Alkohol [9] [vergl. auch 17 β -Acetoxy-3-methoxy-14 β -östra-1,3,5(10)-trien-15 α -ol 7].

Bei der Verbindung 5 tritt das 17-Protonensignal als Triplett mit einer Summe der Kopplungskonstanten von 11 Hz auf, das bei gegebener 17-Konfiguration der Acetoxygruppe den Schluß auf eine 14β -Konfiguration erlaubt.

Das Signal des 15-Protons erscheint als Doppeldublett mit den unterschiedlichen Kopplungskonstanten 10 Hz und 4 Hz. Aus der Summe dieser Kopplungskonstanten [9] und der Abwesenheit einer Wasserstoffbrückenbindung (IR-Spektrum) folgt eine 14β ,15 α -Konfiguration der Substituenten.

Der Acetaminoalkohol 6 weist ebenfalls für das 17-Protonensignal ein Triplett ($\Sigma J = 11$ Hz) auf, das eine 14 β -Konfiguration bei gegebener 17 β -Acetatgruppe anzeigt. Aus dem Doppeldublett des 15-Protonensignals mit den Kopplungskonstanten 9,5 Hz und 4 Hz kann wie bei 5 auf dessen β -Konfiguration geschlossen werden. Die Substituenten weisen somit 14 β ,15 α -Konfiguration auf. Da 6 in physikalischen Konstanten und MS- und ¹H-NMR-Spektrum verschieden von dem 15 β -Acetaminoalkohol 9a ist (der aus 1 durch



Azidspaltung und nachfolgende Reduktion und Acetylierung erhalten wurde) muß ein 14β -Acetamino- 15α -hydroxy-Isomerse vorliegen.

Bei 148,158-Oxido-cardenoliden erfolgt die Öffnung mit starken Nucleophilen wie HCl/Chloroform [10], oder NaN₃/DMSO/Eisessig [3] am C-15 unter Bildung von 15a-substituierten 14β-Hydroxyverbindungen. Bei ähnlichem Verlauf der Ritter-Reaktion sollte aus dem 14 β , 15 β -Epoxid 10 der 15 α --Acetamino-14 β -alkohol 13a entstehen. Durch Umsetzung von 10 mit Acetonitril in Methylenchlorid in Gegenwart von BF₂-Etherat bei 0 °C bildet sich eine blaßgelbe Lösung, die nach Aufarbeitung und Umkristallisation aus Methanol 54% des 15-Ketons 11 ergab [4]. (Durch Reduktion von 11 mit NaBH₄ in Methanol erhält man 63% 17β-Acetoxy-3-methoxy-östra-1,3,5(10)--trien-15 β -ol 12a, das sich alkalisch zum bekannten 15 β ,17 β -Diol 12b [11] verseifen läßt.) Nach Schnellchromatographie der Mutterlauge an Aluminiumoxid lassen sich ca. 20% des ungesättigten Ketons 3 und 15,5% des 15a--Acetamino-14 β -alkohols 13a gewinnen. In parallel durchgeführten Versuchen zeigte sich, daß innerhalb von 10 Minuten 10 mit BF₃-Etherat in Methylenchlorid ohne Zusatz von Acetonitril in ca. 90% Ausbeute zu 11 isomerisiert. Wie im Fall des 14α , 15α -Epoxids 1 läuft die Isomerisierung dem Angriff des Nucleophils den Rang ab.

13a läßt sich nicht mit Acetanhydrid/Pyridin acetylieren. Die Hydroxylfrequenz bei 3573 cm⁻¹ im IR-Spektrum sowie die chemische Verschiebung der 13-Methylprotonen (1,02 ppm) und die Kopplungskonstante für das 17 β -Proton ($\Sigma J = 9$ Hz) im ¹H-NMR-Spektrum lassen auf eine 14 β -Hydroxylfunktion schließen. Unter Annahme einer *trans-diaxialen* Ringöffnung muß sich die Acetaminogruppe in 15 α -Position befinden. Die Verbindung 13a ist mit ihren physikalischen Daten und im R_f -Wert identisch mit einer auf anderem Weg dargestellten Probe (Die Synthese erfolgte aus dem 14 β ,15 β -Epoxid 10 über den 15 α -Azido-14 β -alkohol [12], dessen Reduktion zum Aminoalkohol mit Hydrazinhydrat/Raney-Nickel und nachfolgende Acetylierung mit Acetanhydrid in Pyridin.)

Die Ringöffnung von 15β , 16β -Epoxiden [11, 15] des Östratriens erfolgt mit starken Nucleophilen vorzugsweise am C-16 unter Bildung von 16β -substituierten 15β -Alkoholen [11], während die säurekatalysierte Ringöffnung mit schwächeren Nucleophilen zunächst unter Isomerisierung zu 14,15ungesättigten 16-Hydroxyverbindungen führt, die nachfolgend substituiert werden [13].

Die Ritter-Reaktion des 15β , 16β -Epoxids 14 mit Acetonitril und BF₃-Etherat bei 0 °C ergibt ein Substanzgemisch. Nach der Schnellchromatographie an Aluminiumoxid lassen sich 59% eines nicht trennbaren Gemischs der 8,9-ungesättigten Verbindungen 15a und 15b isolieren. Durch Verseifung des Gemischs entsteht das 16β , 17β -Diol 15c, das nach Acetylierung als 16β , 17β -Diacetat 15d und als Acetonid 16 charakterisiert wurde. Eine weitere Fraktion

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Verbin-			Substitue	nt			(Chemische
dung	C-3	C-14	C-15	C-16	C-17	Δ	Me-13	3-0CH ₃
2	CH_3O	$\beta \mathbf{H}$	=0	-	βΟΑc		1,27	3,70
3	$CH_{3}O$	$\beta \mathbf{H}$	=0			16 - 17	1,25	3,70
4	$CH_{3}O$	$\beta { m H}$	αOH		βOAc	8-9	0,93	3,72
5	$\mathrm{CH}_3\mathrm{O}$	$\beta \mathrm{OH}$	αOH		βΟΑc		0,96	3,69
6	$CH_{3}O$	β NHAc	αOH		βOAc		0,94	3,70
7	$CH_{3}O$	$\beta \mathrm{H}$	αOH		βOAc		0,98	3,71
8	$CH_{3}O$	$\beta \mathrm{H}$	$\beta \mathrm{OH}$		βOAc		1,06	3,70
9a	$CH_{3}O$	αOH	$\beta \mathrm{NHAc}$		βΟΑς		1,08	3,70
11	$CH_{3}O$	αH	=0		βOAc		0,91	3,70
12a	$CH_{3}O$	αH	$\beta \mathbf{OH}$		βOAc		1,08	3,70
13a	$CH_{3}O$	$\beta \mathrm{OH}$	αNHAc		βOAc		1,02	3,70
15c	$CH_{3}O$	βH	8	$\beta \mathrm{OH}$	βOH	8-9	1,05	3,72
15d	$CH_{3}O$	$\beta \mathrm{H}$		βOAc	βΟΑε	8-9	1,00	3,72
16	$CH_{3}O$	$\beta \mathbf{H}$		β -ACETON	ID	8-9	1,02	3,71
18a	CH ₃ O	αH	etaOH	αNHAc	β OAc		1,16	3,70

Table I

* Aufnahme nach Zusatz von Trichloracetylisocyanat (TAI) [14]

(19,5%) der Schnellchromatographie weist im IR-Spektrum eine Acetaminojedoch keine Hydroxylgruppe auf. Im ¹H-NMR-Spektrum der dünnschichtchromatographisch einheitlichen Probe (Molmasse: 383,2135 entspricht $C_{23}H_{29}NO_4$) werden 3 Methylsignale festgestellt die nicht näher untersuchte Doppelbindungsisomere von 16 ξ -Acetamino-17 β -acetoxy-Verbindung 17 darstellen können. Der erwartete 16 α -Acetamino-15 β -alkohol 18a, dessen Dar-

Verschiebungen von (å ppm))			TAL Prolition *	Kopplungskon-	
Ac	15H	16H	17H	OH, NH	andere	TAI-Reaktion*	J (Hz)
2,06			5,05				$J_{ m 16,17}=6~{ m Hz}$
		5,95	7,50				$J_{16,17}=6~\mathrm{Hz}$
2,05	4,46		5,08	1,58		5,65 15 β H; 8,1 NH	$\Sigma J_{15} = 16~{ m Hz}$
2,01	4,30		4,91	1,75		5,02 17 α H; 5,9 15 β H; 8,2 NH	$\Sigma J_{17} = 11~{ m Hz}$
2,06	4,51		5,11	1,62		$5,75 \ 15 \beta H;$ $8,14 \ NH$	$\Sigma J_{17} = 11~{ m Hz}$
2,03	4,60		5,05	1,80		5,67 15βH; 8,29 NH	$egin{array}{lll} arsigma J_{15} = 15 \ { m Hz}; \ arsigma J_{17} = 11 \ { m Hz} \end{array}$
2,08	4,40		4,80	1,70		5,42 15aH; 8,40 NH	$egin{array}{lll} arsigma J_{15} &= 21 \ { m Hz}; \ arsigma J_{17,16} &= 6 \ { m Hz} \end{array}$
1,93; 2,04	4,25		5,29	5,61		8,51 NH	$egin{array}{lll} arsigma J_{15} &= 10 \ { m Hz}; \ arsigma J_{17} &= 15 \ { m Hz} \end{array}$
2,08			5,01				$\varSigma J_{17} = 17~{ m Hz}$
2,02	4,33		4,99	1,85		5,31 15αH; 8,47 NH	$egin{array}{lll} arsigma J_{15} = 11 & \mathrm{Hz}; \ arsigma J_{17} = 16 & \mathrm{Hz} \end{array}$
1,96; 2,08	4,92		5,06	5,84		8,6 NH	$\Sigma J_{17} = 9~{ m Hz}$
		3,63	4,3	2,45		5,1 16aH; 5,5 17aH; 8,7 NH	$J_{ m 17,16}=5~{ m Hz}$
2,00; 2,08		5,35	4,95				$J_{ m 17,16}=5~{ m Hz}$
		4,65	4,00		1,3; 1,47 (CH ₃) ₂ -C $\bigcirc 0-$ 0-		$J_{17,16}=5~{ m Hz};\ J_{16,15}=5~{ m Hz}$
1,97; 2,10	3,90		4,48	1,90		4,3 15αH; 8,4 NH	

stellung auf unabhängigem Wege aus dem 16α -Azido- 15β -alkohol [11] gelang, konnte chromatographisch nicht nachgewiesen werden. Offensichtlich findet primär eine durch BF₃-Etherat katalysierte Ringöffnung des 15β , 16β -Epoxids 10 zu einem 14,15-ungesättigten 16-substituierten Östratrien statt, das sich zu den 8,9-ungesättigten Verbindungen 15a und 15b isomerisiert bzw. durch Acetonitril am C-16 substituiert und nachfolgend isomerisiert wird. Dagegen



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scheint die direkte nucleophile Öffnung von 14 durch Acetonitril nicht abzulaufen. Die Ergebnisse zeigen, daß die Ritter-Reaktion bei den 5-Ring-Epoxiden 1, 10 und 14 kein präparativ günstiger Weg zur Darstellung von *trans*-Acetaminoalkoholen ist. Die gewünschten Verbindungen sind effektiver über die entsprechenden Azidoalkohole zu synthetisieren.

Massenspektren der Acetaminoalkohole

Der massenspektrometrische Fragmentierungsverlauf der neu synthetisierten Acetaminoalkohole 6, 9a, 13a und 18a wird in eindeutiger Weise von den Substituenten im Ring D bestimmt und weist in Abhängigkeit von der Stellung und der Konfiguration der funktionellen Gruppen signifikante Unterschiede auf. Bei den 14-Hydroxy-15-acetaminosteroiden 9a und 13a wird in einer primären Fragmentierungsreaktion Wasser unter Bildung des Fragmentions m/z 383 eliminiert. Ausgehend von diesen dehydratisierten Molekülionen führt der weitere Abbau unter Verlust von Acetamid und Essigsäure zu den Fragmentionen m/z 324 und 264, wobei m/z 264 den Basispeak in den Spektren beider Acetaminoalkohole bildet. Eine primäre Abspaltung von Acetamid oder Essigsäure aus dem Molekülion von 9a und 13a erfolgt nur in geringem Maße. 9a weist nur einen sehr schwachen Molpeak (0,8%) rel. Intensität) auf und kann auf diese Weise von 13a unterschieden werden, dessen Molpeak 6,5% rel. Intensität erreicht. Im Gegensatz zu 9a und 13a ist die primäre Eliminierung von Acetamid aus den Molekülionen der 14- bzw. 16-Acetaminoalkohole 6 und 18a die dominierende Fragmentierungsreaktion. Sie führt zu dem Fragmention m/z 342, das den Basispeak in den Spektren beider Verbindungen darstellt. Durch nachfolgende Abspaltung von Essigsäure und Wasser



Abb. 4

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werden die Bruchstückionen m/z 282 und 264 gebildet. **18a** unterscheidet sich durch den wesentlich höheren Molpeak 47,6% rel. Intensität) von 6 (9,8% rel. Intensität).

Experimenteller Teil

Die Schmelzpunkte sind auf dem Mikroheiztisch nach BOETIUS bestimmt (korrigiert). Die Drehwerte wurden mit einem lichtelektrischen Polarimeter POLAMAT (VEB Carl Zeiss, Jena), falls nicht anders angegeben, in Chloroform ermittelt und auf $[\alpha]_D$ extrapoliert. Die IR-Spektren wurden mit einem Spektralphotometer Specord 75 IR (VEB Carl Zeiss, Jena) in Chloroform aufgenommen. Die Ausführungen der ¹H-NMR Messungen erfolgte in CDCl₃ unter Verwendung von TMS als innerem Standard bei 60 MHz (Jeol, C-60 HL, Tokyo) bzw.

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bei 100 MHz (KRH 100, Zentrum für wiss, Gerätebau der AdW der DDR). Der H-D-Austausch wurde mit CF₂COOD durchgeführt. Die Angabe erfolgt in ppm der δ -Skala. Die Aufnahme der Massenspektren erfolgte mit einem doppelfokussierenden Gerät (JEOL JMS-D 100); Beschleunigungsspannung 3 KV; Direkteinlaß, Probentemperatur 170-180 °C; Ionenquellentemperatur 200 °C; Ionisierungsenergie 75 eV. Die Massenfeinbestimmung wurde bei einer Auflössung von ca. 5000 nach der Peakmatching-Methode mit PFK als Referenzsubstanz durchgeführt. Die präparative Schichtchromatographie (PSC) erfolgte an selbstbeschichteten Platten (Format 20×40 cm) mit Al₂O₂ (VEB Chemiewerk Greiz-Dölau) bei 5 mm Schichtdicke oder an Kieselgel 60 PF254 (MERCK AG) bei 1 mm Schichtdicke. Die Dünnschichtchromatographie erfolgte auf Kieselgel G (MERCK AG) mit den Laufmittelgemischen Methanol/Benzen 1:99 (I); Methanol/Benzen 5:95 (II); Aceton/Benzen 10:90 (III), bzw. an Kieselgel 60 HF254 (MERCK AG) mit dem Laufmittelgemisch Benzen/Aceton/Ethanol 20:5:1 (IV). Die Sichtbarmachung erfolgte durch Besprühen mit verdünnter Phosphorsäure bzw. Vanillin-Schwefelsäure und Erhitzen der Platten auf 140 °C.

Allgemeine Vorschrift zur Umsetzung der 14,15-Epoxide und des 15β,16β-Epoxids des 3-Methoxy-östra-1,3,5(10)-trien-17β-ol-17-acetats mit Acetonitril/BF₂-Etherat

1 g Epoxid 1, 10 oder 14 werden in 30 mL Acetonitril suspendiert. Bei 0 °C wird zur Mischung eine Lösung von 0.4 mL BF3-Etherat in 2 mL Acetonitril gegeben, die Reaktionsmischung bis zur vollständigen Lösung gerührt und bei Raumtemperatur stehengelassen. Der Reaktionsverlauf wird dünnschichtchromatographisch kontrolliert. Nach beendeter Reaktion wird mit Wasser versetzt, mit Benzen oder Ether extrahiert, mit NaHCO₃-Lösung neutral gewaschen und über Na₂SO₄ getrocknet. Das Lösungsmittel wird unter Vakuum verdampft und das Rohprodukt durch Umkristallisation und Chromatographie aufgetrennt.

Reaktionsprodukte von 14a,15a-Oxido-3-methoxy-östra-1,3,5(10)-trien-17\beta-ol-17-acetat (1) mit Acetonitril

Das nach der allgemeinen Vorschrift gewonnene Rohprodukt wird aus Methanol umkristallisiert. Dabei werden 530 mg (53%) 3-Methoxy-17 β -acetoxy-14 β -östra-1,3,5(10)-trien-15-on (2) abgetrennt. F.: 137–139 °C (Methanol). R_f : 0,85 (I.). $[\alpha]_D$: +95° (c = 1). IR: 1605 (Phenyl) 1732 (OAc) mit Schulter 1716 cm⁻¹ (C=O) $C_{21}H_{26}O_4$ (342,4). Ber. C 73,67 H 7,65. Gef. C 74,13 H 7,82%.

Die Mutterlauge wird an Al₂O₃ unter Anwendung von Vakuum chromatographiert. (Länge der Säule 25 cm, Durchmesser 1 cm, Füllmenge an Al₂O₃ 60 g).

Fraktionen: 600 mL Benzen/Petroläther (5:95)

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(Elution von 3) 400 mL Benzen/Petroläther (10:90) (Elution von 4) 600 mL Benzen/Petroläther (25:75) (Elution von 5) 200 mL Benzen/Petroläther (50:50) 400 mL Benzen (Elution von 6) 3-Methoxy-östra-1,3,5(10),16(17)-tetraen-15-on (3). Ausheute: 175 mg (21%). F.: 81-82 °C (Methanol). R_f : 0,90 (I.). $[\alpha]_D$: +330° (c = 1). Aushence: 115 mg (21/6): 11. 01 of 20 (methanol): 11. 050 (11): [α]_D: +550 (e = 1): 1R: 1600 (Phenyl)1695 cm⁻¹ (C=C=C=O). C₁₉H₂₂O₂ (282,40). Ber. C 80,81, H 7,85. Gef. C 81,08, H 7,68%. 3-Methoxy-14 β -östra-1,3,5(10),8(9)-tetraen-15 α ,17 β -diol-17-acetat (4). Ausheute: 30 mg (3%). F.: 140–141 °C (Methanol). R_f : 0,50 (I.). [α]_D: +72° (c = 1). IR: 1603 (Phenyl), 1713 (OAc), 3627 cm⁻¹ (OH). UV: (EtOH) $\lambda_{\text{max}} = 274 \text{ nm}, \epsilon = 4,24.$ C₂₁H₂₆O₄ (324,43). Ber. C 73,67, H 7,65. Gef. C 73,90, H 7,45%. 3-Methoxy-östra-1,3,5(10)-trien- 14β ,15 α ,17 β -triol-17-acetat (5). Ausbeute: 52 mg (5%). F.: 124–127 °C (Ether/Hexan). R_f : 0,40 (I.). $[\alpha]_D$: +66° (c = 1).IR: 1600 (Phenyl), 1715 (OAc), 3630 cm⁻¹ (OH). C₂₁H₂₈O₅ (360,45). Ber. C 69,98, H 7,83. Gef. C 70,10, H 7,55%. 14β -Acetamino-3-methoxy-östra-1,3,5(10)-trien-15 α ,17 β -diol-17-acetat (6). Ausbeute: 70 mg (6%). F.: 207-209 °C (Methanol). Rf: 0,20 (I.); 0,45 (II.); 0,38 (IV.).

 $[\alpha]_{\rm D}: +90^{\circ} (c=1).$ IR: 1650, 3415 (NHCO), 3580 cm⁻¹ (verbreitert, OH). C23H31O5N (401,5). Ber. C 68,80, H 7,78, N 3,48. Gef. C 68,65, H 7,85, N 3,20%.

Reduktion des 3-Methoxy- 17β -acetoxy- 14β -östra-1,3,5(10)-trien-15-ons (2)

1 g 2 werden in 50 mL Methanol mit 0,5 g NaBH4 innerhalb von 30 Minuten bei Raumtemperatur reduziert. Durch Verdünnen mit Wasser fällt ein Rohprodukt aus, das abgesaugt und aus Methanol umkristallisiert wird. Man erhält 450 mg (45%) 3-Methoxy-14ß-östra-1,3,5(10)-trien-15α,17β-diol-17-acetat (7). Die Mutterlauge wird durch PSC an Al₂O₃ mit dem

1,5,5(10)-trien-152,17)-trien-157,17)-trienet (7). The Mutterlauge wird durch F5C an Al₂O₃ mit dem Laufmittelgemisch Benzen/Aceton (4 : 1) getrennt. Dabei lassen sich weitere 270 mg (27%) 7. F.: 170–172 °C (Ether/Hexan). $R_{f^{2}}$ 0,82 (IV.). $[\alpha]_{D^{2}}$ +119° (c = 1). IR: 1602 (Phenyl), 1713 (OAc), 3613 cm⁻¹ (OH). $C_{21}H_{24}O_{4}$ (344,4). Ber. C 73,24, H 8,19. Gef. C 73,04, H 8,31%, und 148 mg (15%) 3-Methoxy-14 β -östra-1,3,5(10)-trien-15 β ,17 β -diol-17-acetat (8) isolieren. F.: 147–148 °C (Ether/Hexan). $R_{f^{2}}$ 0,64 (IV.). $[\alpha]_{D^{2}}$ +98° (c = 1). IR: 1603 (Phenyl), 1716 (OAc), 3603 cm⁻¹ (OH). $C_{21}H_{24}O_{4}$ (344,4). Ber. C 73,24, H 8,19. Ber. C 73,40, H 8,03%.

Darstellung von 15β -Acetamino-3-methoxy-östra-1,3,5(10)-trien-14 α ,17 β --diol-17-acetat (9a)

1 g 17β -Acetoxy-15 β -azido-3-methoxy-östra-1,3,5(10)-trien-14 α -ol (hergestellt aus 1 durch Ringöffnung mit Natriumazid in DMSO/Eisessig [11, 12]) wird in 20 mL Ethanol mit 0,3 g Raney-Nickel und 2 mL Hydrazinhydrat (85%) 5 Minuten unter Siedehitze behandelt. Nach Abtrennung des Katalysators wird die Lösung unter Vakuum eingeengt und das verbleibende blaßgele Öl (890 mg, 95%) mit 3 mL Acetanhydrid in 5 mL Pyridin bei Raumtemperatur acetyliert. Die Reaktionsmischung wird in Wasser gegossen, das ausgefallene Produkt nach einiger Zeit abgesaugt, mit Wasser gewaschen und aus Ethanol umkristallisiert. Man erhält 585 mg (59%) **9a**. F.: 249–253 °C (Ethanol). *Rf*: 0,46 (IV.). [α]_D: +55° (c = 1). IR: 1608 (Phenyl). 1667 (NHC=O), 1732 (OAc), 3460 (NH), 3600 cm⁻¹ (OH). $C_{21}H_{31}NO_5$ (401,5). Ber. C 68,81, H 7,78, N 3,49. Gef. C 68,63, H 7,63, N 3,60%.

Durch Verseifung von **9a** mit 5% iger methanolischer KOH entsteht innerhalb von 10 Minutes das 15β -Acetamino-3-methoxy-östra-1,3,5(10)-trien-14 α ,17 β -diol (**9b**). F.: 222–225 °C (Aceton). $[\alpha]_{D}$: +78° (c = 1).

Reaktionsprodukte von 14 α ,15 α -Oxido-3-methoxy-östra-1,3,5(10)-trien-17 β -ol-17-acetat (1) mit BF₃-Etherat in Methylenchlorid

1 g 1 wird in 20 mL Methylenchlorid innerhalb von 10 Minuten bei Raumtemperatur mit 0,4 mL BF₃-Etherat umgesetzt. Nach Zugabe von NaHCO₃-Lösung wird mit Methylenchlorid extrachiert, mit Wasser gewaschen und über Na₂SO₄ getrocknet. Nach Verdampfen des Lösungsmittels unter Vakuum wird der Rückstand aus Methanol umkristallisiert. Man erhält 350 mg (35%) 2. Die Mutterlauge wird durch PSC an Kiseelgel PF₂₅₄ mit Benzen/Aceton (9:1) aufgetrennt. Es lassen sich weitere 19% 2, 82 mg (8%) 3 und 210 mg (21%) 4 isolieren.

Reaktionsprodukte von 14β , 15β -Oxido-3-methoxy-östra-1, 3, 5(10)-trien-- 17β -ol-17-acetat (10) mit Acetonitril

Das nach der allgemeinen Vorschrift gewonnene Rohprodukt wird aus Methanol umkristallisiert. Man erhält 315 mg (54%) 17 β -Acetoxy-3-methoxy-östra-1,3,5(10)-trien-15-on (11). F.: 157–159 °C (Methanol). R_f : 0,85 (I.). $[\alpha]_D$: +80° (c = 1) (*Lit.*: [5] F.: 156–158 °C; $[\alpha]_D$: +82°).

IR: 1733 cm⁻¹ (OAc und C=0).

Die Mutterlauge wird wie bei der Reaktion von 1 beschrieben chromatographiert. Fraktionen: 600 mL Benzen/Petrolether (5:95)

(Elution von 3, 165 mg (20%)

200 mL Benzen/Petrolether (10:90)

200 mL Benzen/Petrolether (50:50)

(Elution von 13a)

15α-Acetamino-3-methoxy-östra-1,3,5(10-trien- 14β ,17β-diol-17-acetat (13a).

Ausbeute: 187 mg (16%). F.: 213-215 °C (Aceton/Hexan). $R_f: 0.40$ (IV.). $[\alpha]_D: +65^{\circ}$ (c = 1). IR: 1611 (Phenyl), 1677 (NHC=0), 1740 (0Ac), 3440 (NH), 3753 cm⁻¹ (OH).

C₂₃H₃₁NO₅ (401,5). Ber. C 68,81, H 7,78, N 3, 49. Gef. C 68,38. H 7,85, N 3,58%.

Reduktion des 3-Methoxy-17β-acetoxy-östra-1,3,5(10)-trien-15-ons (11)

300 mg 11 werden in 20 mL Methanol mit 150 mg NaBH₄ bei Raumtemperatur innerhalb von 20 Minuten reduziert. Das mit Wasser ausgefällte Produkt wird abgesaugt, getrocknet und aus Hexan/Ether umkristallisiert. Ausbeute: 218 mg (63%) 3-Methoxy-östra-1,3,5(10)-trien-15 β ,17 β -diol-17-acetat (12). F.: 133-135 °C. R_f : 0,66 (IV.). [α]_D: +7° (c = 1).

IR: 1604 (Phenyl), 1725 (OAc), 3605 cm⁻¹ (OH).

C21H24O4 (344,40). Ber. C 73,24, H 8,19. Gef. C 73,32, H 8,29%.

15α -Acetamino-3-methoxy-östra-1,3,5(10)-trien-14 β ,17 β -diol-17-acetat (13a)

Die Darstellung erfolgt analog der Vorschrift unter **9a**. Das Rohprodukt wird aus Aceton/Hexan umkristallisiert. Man erhält 320 mg (32%) **13a**. F.: 213-215 °C. R_f : 0,40 (IV.). $[\alpha]_D$: +65° (c = 1).

0,5 g 13a werden analog der Vorschrift von 9b verseift und aus Methanol umkristallisiert. Ausbeute: 210 mg (47%) 15 α -Acetamino-3-methoxy-östra-1,3,5(10)-trien-14 β ,17 β -diol (13b). F.: 286–290 °C (Methanol). [α]_D: + 85° (c = 1; DMSO).

Reaktionsprodukt von 14β , 15β -Oxido-3-methoxy-östra-1, 3, 5(10)-trien-17 β -ol-17-acetat (10) mit BF₃-Etherat in Methylenchlorid

1 g 10 wird in 20 mL Methylenchlorid innerhalb von 10 Minuten bei Raumtemperatur nit 0,4 mL BF₃-Etherat umgesetzt. Die Aufarbeitung ist analog wie bei der Umsetzung von 1. Man erhält 900 mg (90%) 11.

Reaktionsprodukte von 15β , 16β -Oxido-3-methoxy-östra-1, 3, 5(10)-trien- 17β -ol-17-acetat (14) mit Acetonitril

Das nach der allgemeinen Vorschrift gewonnene Rohprodukt wird wie bei der Reaktion von 1 beschrieben chromatographiert.

Fraktionen: 500 mL Benzen/Petrolether (10:90)

(Elution unpolarer Anteile)

500 mL Benzen/Petrolether (50:50)

500 mL Benzen

(Elution eines untrennbaren Gemisches von 15a, 15b 590 mg (59%))

300 mL Benzen/Chloroform (75:25)

(Elution einer nicht charackterisierten Acetamino-Verbindung 17)

3-Methoxy-östra-1,3,5(10),8(9)-tetraen-16β,17β-diol-diacetat (15d)

342 mg 15a und 15b, 2 mL Pyridin und 2 mL Acetanhydrid werden bei Raumtemperatur über Nacht stehengelassen. Danach wird die Reaktionsmischung in Wasser gegossen, das ausgefallene Produkt nach einiger Zeit abgesaugt, mit Wasser gewaschen und aus Methanol/ Wasser umkristallisiert. Ausbeute: 350 mg (91%). F.: 110-112 °C. R_f: 0,80 (I.). [\alpha]_D: +90° (c = 1).

IR: 1610 (Phenyl), 1740 cm⁻¹ (OAc).

C23H28O5 (384,47). Ber. C 71,86, H 7,34. Gef. C 71,50, H 7,46%.

3-Methoxy-östra-1,3,5(10),8(9)-tetraen-16 β ,17 β -diol (15c)

342 mg 15a und 15b, 10 mL Methanol und 0.1 g NaOCH3 werden bei Raumtemperatur über Nacht stehengelassen. Danach wird die Reaktionsmischung mit 1n HCl neutralisiert und in Wasser gegossen. Das ausgefallene Produkt wird abgesaugt und aus Aceton/Wasser um-kristallisiert. Ausbeute: 280 mg (93%). F.: 109–111 °C. R_f : 0,45 (III.). $[\alpha]_D$: +92° (c = 1). IR: 1610 (Phenyl), 3610 cm⁻¹ (OH).

C₁₉H₂₄O₃ (300,40). Ber. C 75,91, H 8,05. Gef. C 75,85, H 7,90%.

16β , 17β -Isopropylidendioxy-östra-1, 3, 5(10), 8(9)-tetraen-3-methylether (16)

300 mg 15c werden in 20 mL Aceton und einigen Tropfen BF3-Etherat bei 20 °C umesetzt. Nach 6 Stunden wird NaHCO3-Lösung und Benzen zugefügt. Die benzolische Phase wäscht man mit Wasser. Nach Trocknen über Na2SO4 wird das Lösungsmittel im Vakuum eingeengt und das bleibende hellblaue Öl in Methanol aufgenommen. Beim Abkühlen kristallisierten farblose Prismen. Ausbeute: 290 mg (85%). F.: 118-120 °C. R_f : 0,90 (I.). $[\alpha]_D$: +98° (c = 1).

IR: 1610 cm⁻¹ (Phenyl).

C22H28O3 (340, 46). Ber. C 77,62, H 8,29. Gef. C 77,50, H 8,05%.

Darstellung von 16a-Acetamino-3-methoxy-östra-1,3,5(10)--trien-15 β ,17 β -diol-17-acetat (18a)

500 mg 16 α -Azido-3-methoxy-1,3,5(10)-trien-15 β ,17 β -diol-17-acetat [11] werden analog der Vorschrift unter 9a reduziert und mit Acetanhydrid in abs. Ether acyliert. Die mit NaHCO3-Lösung neutralisierte Reaktionsmischung ergibt nach Etherextraktion 356 mg (68%) eines Öls. Durch PSC an Kieselgel mit dem Laufmittel Benzen/Aceton/Ethanol (20:5:1) werden 312 mg 18a als farbloser Schaum erhalten. R_{f} : 0,43 (IV.). $[\alpha]_{D}$: $+15^{\circ}$ (c = 1, DMSO). IR: 1603 (Phenyl), 1647 (NHC=O), 1713 (OAc), 3400 (NH), 3500 cm⁻¹ (OH).

250 mg 18a werden analog der Vorschrift 9b verseift. Mit Ether : Benzen (1:1) werden 210 mg (75%) 18b isoliert. F.: 243-246 °C (Methanol). $[\alpha]_D$: +50° (c = 1, DMSO).

IR: 1605 (Phenyl), 1653 (NHC=O), 3425 (NH), 3600 cm⁻¹ (OH).

Wir danken Prof. PONSOLD und Dr. SCHÖNECKER für die Diskussion der Ergebnisse Frau H. DRAFFEHN und Frau Cs. HORVÁTH für experimentelle Mitarbeit sowie Frau Dr. B. Bozóki für die mikroanalytische Arbeit.

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Lable II	Ta	b	le	п
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Relative Intensitäten einiger charakteristischer Fragmentionen von Massenspektren der Acetaminoalkohole 6, 9a, 13a und 18a in [%] (Basispeak $\triangleq 100\%$)

m/z	6	9a	13a	18a	
401	9,8	6,5	0,8	47,4	M+
383	10,2	10,0	14,7	3,5	$M^+-{ m H_2O}$
342	100,0	2,0	< 0,5	100,0	$M^+-{ m CH_3CONH_2}$
341	7,1	1,5	0,7	7,4	$M^+ - \mathrm{CH_3COOH}$
324	7,5	41,5	21,4	3,5	$M^+ - \mathrm{H_2O-CH_3CONH_2}$
323	4,6	4,9	4, 4	10,9	$M^+-{ m H_2O-CH_3COOH}$
282	37,0	5,4	2,3	39,7	$M^+ - \mathrm{CH_3CONH_2} - \mathrm{CH_3COOH}$
264	44,2	100,0	100,0	23,0	$M^+ - \mathrm{CH_3CONH_2} - \mathrm{CH_3COOH} - \mathrm{H_2O}$

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OPTIMAL OPERATION OF HYDRODESULFURIZATION REACTOR BASED ON A KINETIC MODEL

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The validity of formal power-law kinetic models for the description of hydrodesulfurization reactions was tested on experimental data obtained on two types of laboratory and pilot plant reactors. An objective function for characteristic production plant is described and optimal conditions for the production of the low sulfur fuel oil are determined numerically.

Introduction

Hydrodesulfurization is widely used for removal of sulfur, nitrogen and other impurities from the oil fractions ranging from light to heavy distillates. The progress in the effective catalysts development enables now to operate the reactors at lower temperatures and pressures and higher space velocities for light distillates, but process is feasible for high average molecular weight fractions (boiling point between 350-550 °C) also [1, 2]. However, the operating conditions for high molecular fractions, i.e. pressure, hydrogen specific consumption, catalyst coking etc., are more severe, also due to a more complicated nature of the sulfur components present. The economy of the desulfurization is crucially dependent on the hydrogen consumption and energy requirements. The specific consumption of hydrogen increases with the increasing temperature and pressure in the reactor. The determination of optimal operating conditions for desulfurization reactor requires the knowledge of the kinetics of desulfurization. The aim of this work was to verify the validity of formal power-law kinetic models proposed in the literature by comparison with experimental data obtained in our laboratory, formulate proper objective function for characteristic production plant and evaluate optimal conditions for the production of low sulfur fuel oil.

As the prices of raw materials and energy vary drastically in the current years and more effective catalysts are developed, the optimal operating conditions should be reevaluated more often even for plants which are already for a number of years on stream.

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Fig. 1. Hydrodesulfurization laboratory reactor. Experimental set up: 1 – pressure container, 2 – reduction valve, 3 – high pressure flow meter, 4 – recorder, 5 – preheater, 6 – electric oven (heater), 7 – reactor, 8 – temperature control and recording, 9 – resistance thermometer, 10 – thermocouple, 11 – feed storage, 12 – pump, 13 – cooler, 14 – separator, 15 – sample removal, 16 – gas meter, 17 – gas removal

Feed	Vacuum gas oil	First oil fraction	Second oil fraction	Third oil fraction
Density (20 °C)	0.875	0.903	0.933	0.939
ASTM °C	250	332	368	360
10% vol.	276	415	448	461
20% vol.	283	444	470	488
30% vol.	291	461	486	516
40% vol.	301	474	498	533
50% vol.	308	487	506	542
60% vol.	315	494	513	551
70% vol.	319	504	522	556
80% vol.	325	512	535	572
90% vol.	335	519	564	586
End point $^{\circ}C/^{0}_{0}$ vol.	352/98	526/99	584/97	604/94
Sulfur content % mass	1.560	1.770	1.792	2.260
Nitrogen content, ppm	213	870	1.569	1.677
Basic nitrogen, mg(NH ₃)L	65	295	374	677
Molecular weight	256	408	462	550
Flash point, °C	136	198	246	250

Table I

Experimental

Experimental data on desulfurization of various crude oil distillates were obtained in two types of laboratory and pilot plant reactors. The first reactor, of the laboratory size, had the volume of the bed of catalyst (diameter 0.6-0.8 mm) equal to 5 cm³. The scheme of the experimental set up is shown in Fig. 1. Pure hydrogen was used in a one flow-through arrangement.

The second reactor, with the volume of catalyst equal to 200 cm^3 is shown schematically in Fig. 2. The maximum temperature differences in the laboratory reactor were equal to $3 \,^{\circ}\text{C}$, and were always less than $5 \,^{\circ}\text{C}$ in the pilot plant reactor. Mass balances of liquid and gaseous reaction products could be made in both reactors.



Fig. 2. Pilot plant hydrodesulfurization reactor. 1 — feed storage, 2 — high pressure pump, 3 — reduction valve, 4 — hydrogen inlet, 5 — thermocouple, 6 — pressure gauge, 7, 11, 12, 18, 19 — valves, 8 — high pressure separator, 9 — reduction valve, 10 — gas meter, 14 electric oven (heater), 15 — cast iron block, 16 — reactor, 17 — temperature control and recording, 24 — catalyst, 25 — preheater

The feed consisted from the vacuum distillates obtained from the Romaschkino crude oil and characteristics are given in Table I. After activation of the catalyst and stabilization of its activity in the stream of constant sulfur (2.6%) gas oil, the experiments were performed in both reactors. The on-stream time for given experimental conditions was 8 hours in the laboratory reactor and 48 hours in the pilot plant reactor. Sufficient time for the stabilization of reaction conditions between individual experimental runs was allowed. The range of **ex**perimental condition is given in Table II.

The catalyst CHEROX 36-01 (MoO₃-CoO, surface area 205 m²/g) was used in the reactor.

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	Laboratory reactor	Pilot plant reactor
Pressure MPa	4.9	4.9; 9.8
Temperature °C	300, 340, 360, 380, 400, 420	340, 360, 380, 400, 420
LHSV hour ⁻¹	0.5 - 6	0.5 - 3
Ratio H ₂ /CH m _N /m ³	350	300

Evaluation of experimental results

Power-law kinetics relation $r = Kx_s^n$ was considered for the rate of desulfurization reaction. Let us denote: $-x_{so}$ – mass fraction of sulfur in the feed, x_s – mass fraction of sulfur in the reaction product, $c = 1 - x_s/x_{so}$ conversion, n – overall order of reaction, K – reaction velocity constant, LHSV – liquid hour space velocity. Then on integrating the balance equation for isothermal plug flow reactor we obtain

$$c = 1 - \left[\frac{\text{LHSV}}{(n-1)x_{\text{so}}^{n-1}K + \text{LHSV}}\right]^{\frac{1}{n-1}}$$
(1)

From the experiments the set of values $x_s = x_s$ (LHVS) were available. The kinetic parameters, K and n were then for individual feedstocks evaluated by nonlinear regression. Combined gradient and Gauss—Newton techniques were used. For the evaluation of the temperature dependence of the reaction velocity constant

$$K = \exp\left(A - E/RT\right) \tag{2}$$

all the data for a particular feedstock were evaluated.

Reactor model

Comparison of the experiments conducted in the laboratory pilot plant and industrial (process size) reactors have shown, that agreement in the values of conversion is satisfactory. Estimates of conversion based on the laboratory and pilot plant data were sometimes conservative (conversion in the process plant reactor was higher, maximum difference was equal to 14% rel, in dependence on the feedstock quality and reaction conditions used). We have considered, that process is isothermal (average temperature rise in the industrial reactors is 4-6 °C) and assumed further, that the catalyst is deactivated only by coking, with the rate of deactivation dependent on temperature only. The poisoning by metals present in the vacuum gas oil was neglected.

Objective function

Objective function necessary for calculation of the optimal process conditions was constructed from the total plant expense and plant investment costs. These are based on mass and energy balances.

Mass balance for the consumption of feedstock G (t/year) — (vaccum gas oil) is in the form:

$$G = M + x_{\rm po}m + x_{\rm Lb}m, \qquad (3)$$

$$m = \frac{1}{x_{\rm to}} \frac{x_{\rm so} - x_{\rm sp}}{x_{\rm so} - x_{\rm s}} M. \qquad (4)$$

Here M is the required mass of the fuel oil with sulfur content x_{sp} (mass fraction), m — mass of the reactor feedstock (t/year) x_{to} , x_{po} , x_{Lb} — mass fractions of the fuel oil, gas oil, light gasoline, respectively, in the liquid reaction product,

 x_{so} — sulfur mass fraction in the feedstock,

 $x_{\rm s}$ — sulfur mass fraction in the reaction product,

 $x_{\rm sp}$ — required value of the sulfur mass fraction in the fuel oil.

Gasification of the feedstock is not included - the cost of the feedstock and the value of the resulting fuel gas are considered equal.

Overall hydrogen consumption (H in N m³ t⁻¹) depends on its consumption tion for the formation of H₂S (depends on conversion) and on the consumption for feedstock cracking and hydrogenation of aromatic hydrocarbons (depends on the reaction temperature). The volume (V_{cat}) and consumption (S_{cat}) of a catalyst depend on reaction conditions (temperature T, conversion c), as can be calculated from Eq. (5)

LHSV =
$$\frac{\exp{(A - E/RT)} \cdot (n - 1)x_{so}^{n-1}}{1/(1 - c)^{n-1} - 1}$$
 (5)

Operating time, OT, (hours/year) is a function of temperature

$$\mathbf{OT} = \mathbf{OT}(T) \tag{6}$$

Production rate, PR, of the product is defined as

$$PR = m/OT.$$
(7)

Feedstock cracking expressed as mass ratio of the fuel gas produced over mass of the feedstock consumed, Y, is a function of temperature

$$Y = Y(T) \,. \tag{8}$$

The volume of catalyst V_{cat} (m³) is defined as

$$V_{\rm cat} = \frac{\rm PR}{(1-Y)\,\varrho_{\rm L}\,\rm LHVS} \tag{9}$$

where ρ_L is feedstock density (kg m⁻³).

Life-time of the catalyst, LT (years) is also a function of temperature

$$LT = LT(T). (10)$$

The catalyst comsumption, S_{cat} (t/t of reaction product)

$$S_{\text{cat}} = \frac{V_{\text{cat}} + (1 - Y)}{\text{LT} \cdot m} \,. \tag{11}$$

Inhibitor comsumption - CI (t/year) can be calculated from the relation

$$CI = CIm/(1 - Y).$$
(12)

Energy balances

Electricity, E (KW) is a function of hydrogen consumption and of the production rate

$$E = E(PR, H). \tag{13}$$

Steam, ST (t/hour) is a function of the production rate only

$$ST = ST(PR), \qquad (14)$$

similarly as water consumption, WT (m³/hour),

$$WT = WT(PR) \tag{15}$$

and fuel consumption, F (GJ/hour)

$$\mathbf{F} = \mathbf{F}(\mathbf{PR}) \,. \tag{16}$$

Investment costs relations for individual equipments in the process plant (cf. Fig. 3) were used in the form [4]. Reactor, R (monetary unit)

$$R = R(V_{\text{cat}}/V_{\text{cats}})^{0.8}$$
(17)

(here V_{cats}) denotes standard catalyst volume).

Furnace, F (monetary unit)

$$F = F \left(\frac{\mathrm{PR}}{(1-Y) \mathrm{PR}_{\mathrm{s}}} \right)^{0.6} \tag{18}$$

where PR_s is standard production rate.

Heat exchanger, E (monetary unit)

$$E = E(A/A_{\rm s})^{0.62} \tag{19}$$



Fig. 3. Simplified process scheme

where A_s is standard heat-exchange area. For all other equipments the power in the relations similar to (17-19) was taken equal to 0.6.

Total expenses including depreciation are then composed from the expenses for: raw materials, hydrogen, catalyst, corrosion inhibitor, direct labor, supervision, utilities, electricity, steam, water, fuel indirect costs (related to direct labor), maintenance (0.05 of the plant investment and depreciation 0.1 of the investment costs).

Formulation of the objective function

Required amount of the low sulfur fuel can be produced by two ways (cf. Fig. 3)

a) all vacuum gas oil desulfurized to required sulfur content,

b) part of the vacuum gas oil is desulfurized to lower sulfur content in such a way, that mixture of desulfurized and fresh feedstock has required sulfur content.

The aim of optimization was to calculate conditions for optimal investment utilization. The extreme of the gross return rate -P(%) was computed:

$$P = \frac{\text{Net profit (after taxes)}}{\text{plant investment + working capital}} 100 (\%).$$
(20)

Results and Discussion

Comparison of experimental and calculated data

The reaction rate parameters for conditions given in Table II and also data given in the literature [3] were evaluated in such a way, that we have obtained

a) n, k – for every level of temperature considered

b) n, A, E -for given range of temperatures.

Very satisfactory agreement was found for the values of n(a) based on the data obtained in our laboratory and the data published by the authors from Nippon Mining Co. [3].

The difference between experimental and computed values was both in cases a) and b) less that 7% rel. Hence the power-law kinetics and resulting kinetic parameters could be used in evaluation of optimal reactor operation conditions.

We have also tested the magnitude of error in cases, where only the experimental values at lowest and highest considered temperatures were used for evaluation of the reaction parameters. The vacuum gas oil [3] with the sulfur content 1.73% (mass %) and temperatures ranging from 340 to 380 °C were considered. The results are given in Table III. We can infer from the

$_{\rm h^{-1}}^{\rm LHVS}$	measured	Relative error (%)			
	$(t = 360 ^{\circ}\mathrm{C})$	$t = 360 ^{\circ}\text{C}$	$t = \langle 340, 380 \ ^{\circ}\text{C} \rangle$	$t = \langle 360, 380 \circ C \rangle$	
1.015	0.948	-0.5	-0.8	-1.02	
2.036	0.890	-0.5	-0.1	-0.5	
2.978	0.821	-1.8	2.1	2.6	
4.580	0.769	-0.9	0.2	1.1	

Table III

Table, that the differences observed using boundary points only are quite small. Hence in this case the experiments could be performed only at the limiting conditions with resulting material, energy and labor savings.

Optimization

Total expense and plant investment costs were computed using mass and energy balances given above. Objective function in the form of the gross return rate (GRR) was formed and expressed as a function of reaction temperature T and conversion c. Search for extremum then used numerical techniques. The optimal conditions depend on the properties of the feedstock, required sulfur content in the fuel oil, costs of raw materials, energy and equipment. Some results of the computation are shown in Table IV. The same feedstock quality ($x_{so} = 0.019$) and different costs of the feedstock were considered at varying requirements on the final fuel oil sulfur content (x_s). The results show large variations for the gross return rate for optimal process conditions (which are within the range of common process values).

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x_{sp}	Cost	Mass fraction	Reaction temperature	GRR, rel. %
0.005	100	0.00263	385.5	100
0.005	110	0.00297	375.3	38.56
0.005	115	0.00322	369.1	10.74
0.01	100	0.00227	392.8	100
0.01	110	0.00260	382.4	44 82
0.01	115	0.00283	376.2	19.94

Table IV

Conclusion

Kinetic parameters in the power-law type equation describing the rate of hydrodesulfurization can be evaluated from limited laboratory or pilot plant experiments. The optimal reactor operating conditions can be then calculated with resulting savings.

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PREPARATIONS AND PROPERTIES OF SOME COMPLEX COMPOUNDS OF THORIUM NITRATE WITH ORGANIC LIGANDS

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The interaction of thorium nitrate with some organic ligands was investigated. The effect of the anionic part of the metal compound on the nature and composition of the formed complexes was discussed. Study of the infrared spectra measured between 4000 and 650 cm⁻¹ and thermal analyses in the range 25-800 °C were carried out. Conductivity measurements for the soluble complexes were performed.

Introduction

Thorium nitrate forms a series of double salts of the type $Th(NO_3)_4$, $2 M^I NO_3 \cdot nH_2O$, where $M^I = NH_4$, K, Rb or Cs. These compounds resemble those of Ce(IV) and may contain $[Th(NO_3)_6]^{-2}$ anion. A second series, $Th(NO_3)_4$, $2 M^{II}(NO_3)_2 \cdot 8 H_2O$ is formed with bivalent metal ions, where M^{II} is Mg, Zn, Ni or Co [1]. The Mg salt has been shown to contain 12 coordinated anions with chelated NO_3 groups [2].

It is well established that many transition metal nitrates form complexes with organic ligands containing nitrogen or oxygen atoms [3-8]. However, the interaction of ligands with thorium nitrate has been little investigated [9].

It has been reported that thorium nitrate reacts with 1,2-diethoxy ethane and antipyrine to give the complexes $Th(NO_3)_4$, $3 C_6H_{14}O_2$, $3 H_2O$ and $Th(NO_3)_4 \cdot 5 C_{11}H_{12}N_2O$, respectively. The coordination number of thorium was not obvious in the two cases.

In the present communication, the complexes formed between thorium nitrate and some oxygen- and nitrogen-containing ligands were studied. The ligands were those described in the experimental part.

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Experimental

Material and Methods

Thorium nitrate hexahydrate and tetrahydrate, BDH analar grade, were used without further purification.

Organic solvents were dried and purified by the conventional methods [10].

Infrared spectra were recorded (in nujol or KBr) using a Unicam SP 200 G infrared spectrophotometer. Calibration of frequency reading was made with a polystyrene film. Conductivities were measured using an electronic switchgear bridge model MC-2 with balance indicator, details and methods of calculation have been given before [11]. Thermal analyses techniques was as previously mentioned [12, 13].

Analyses of carbon, hydrogen and nitrogen were carried out in the Microanalytical Laboratory of El-Nasr Company. Analysis of phosphorus was determined by A. Bernhardt, Mulheim/Ruhr, FRG.

Organic ligands

Some of the aromatic derivatives of nitrogen and phosphorus were prepared by the methods described previously [8, 12]. The other ligands used were analar grade materials.

Preparation of the complex compounds

Equimolar amounts of thorium nitrate and the ligand solutions were mixed well in ethyl acetate, EtAc, as a solvent. The product was filtered, washed with the solvent and dried, and then subjected to analysis and physico-chemical investigations. It was found that using an excess of the organic ligand improved the yield, but did not affect the coordination number of the formed complex.

Results

The compound obtained in the reaction of equimolar amounts of 1,2-bis-(diphenylphosphino) ethane, DiPhOS ethane, and thorium nitrate was proved by analysis and ir spectrum not to be the diphenylphosphino ethane complex but the corresponding dioxide adduct, $Th(NO_3)_4$, 1.5 DiPhOS ethane dioxide, which decomposed at 180–190 °C and melted at 200 °C. An authentic sample of this complex, $Th(NO_3)_4$, 1.5 DiPhOS ethane dioxide, was obtained on using DiPhSO ethane dioxide as a ligand.

Attempted preparation of complexes of thorium nitrate with diphenylphosphino ethane or the corresponding diphosphine disulphide were unsuccessful, and the ligand in the latter case was recovered unchanged. This is in agreement with the earlier findings [5, 6].

The reactions of $\text{Th}(\text{NO}_3)_4$ with dimethyl bipyridyl, DM-bipy, and tripyridyl, tripy, in ethyl acetate applying the mole ratios 1:1 and 1:2, gave complex compounds of the formula, $\text{Th}(\text{NO}_3)_4 \cdot 1.5$ L, where L stands for the organic ligands used.

Complexes of the type, $\text{Th}(\text{NO}_3)_4 \cdot 2 \text{ L} \cdot n\text{H}_2\text{O}$ were obtained with dimethyl-*o*-phenanthroline; DM-phen, bipyridyl; bipy, pyrazine and piperidine; pipy, where *n* 6 or 4. Recrystallisation of the products obtained with

pyridine-N-oxide and o-phenanthroline, phen, from ethyl acetate gave the complexes $Th(NO_3)_4 \cdot 2py-N$ -oxide \cdot EtAc and $Th(NO_3)_4 \cdot 2phen \cdot 2$ EtAc.

The complex compounds obtained during the present work are white crystalline compounds stable on air and insoluble in most organic solvents tried, except those used in the conductivity measurements. The only water-soluble complex obtained was that of picolinic acid, $Th(NO_3)_4 \cdot 4$ picolinic $\cdot 4 H_2O$.

Analytical data are given in Table I.

Discussion

Infrared Spectra

The infrared absorption spectrum of thorium nitrate tetrahydrate (Fig. 1) shows six absorption bands in the region 4000-650 cm⁻¹. The bands at 1550-1490 cm⁻¹ (v_1), 810 cm⁻¹ (v_6), 1040-1030 cm⁻¹ (v_3), 1310-1280 cm⁻¹ (v_4), 745 cm⁻¹ (v_3) and 705 cm⁻¹ (v_5). Absorption by water [14] occurs in the region 3500-3100 cm⁻¹ and at 1630 cm⁻¹ (Fig. 1).

The mode of coordination of the nitrate ion, and particularly the relation between this and its infrared spectrum, has been subject of much discussion [15].

Thorium nitrate forms complex compounds with oxygen donors [5]. A comprehensive review of this subject is given recently by CASELLATO [16]. UEKI *et al.* [17] have studied the X-ray analysis of $Th(NO_3)_4 \cdot 5 H_2O$ and concluded that the thorium metal is within bonding distance of eleven oxygen atoms, three from water molecules and eight from four nitrate groups which function as bidentate ligands.

MAZHAR-UL-HAOUE *et al.* [18] have studied in detail the crystal and molecular structure of the complex formed between thorium nitrate and triphenyl phosphine, $Th(NO_3)_4 \cdot 2 Ph_3PO$ and they came to the conclusion





	Formula	Fou	Found/Required			
· · · · · · · · · · · · · · · · · · ·	Formula	C	Н	\mathbf{N}/\mathbf{P}		
$\mathrm{Th}(\mathrm{NO}_3)_4 \cdot 1.5 \mathrm{~DiPhOS}$ ethane dioxide	$\rm C_{39}H_{36}N_4O_{15}P_3Th$	41.5 41.6	$3.5 \\ 3.2$	$8.2 \\ 8.3$		
$Th(NO_3)_4 \cdot 2phen \cdot 2EtAc$	$\rm C_{32}H_{32}N_8O_{16}Th$	$\begin{array}{c} 36.2\\ 37.8\end{array}$	$3.2 \\ 3.2$	$\begin{array}{c} 10.9\\11.0\end{array}$		
$Th(NO_3)_4 \cdot 2 DM$ -phen $\cdot 4 H_2O$	$\rm C_{28}H_{32}N_8O_{16}Th$	$\begin{array}{c} 34.3\\ 34.7\end{array}$	$3.3 \\ 3.3$	$\begin{array}{c} 11.0\\ 11.6\end{array}$		
$Th(NO_3)_4 \cdot 2bipy \cdot 4 H_2O$	$\rm C_{20}H_{24}N_8O_{16}Th$	$27.8 \\ 27.8$	$3.1 \\ 2.8$	$\begin{array}{c} 12.3 \\ 13.0 \end{array}$		
$Th(NO_3)_4 \cdot 1.5$ -DM-bipy	$\rm C_{18}H_{18}N_7O_{12}Th$	$27.7 \\ 28.5$	$2.8 \\ 2.4$	$\begin{array}{c} 12.6 \\ 12.9 \end{array}$		
$Th(NO_3)_4 \cdot 1.5 tripy$	$\rm {}^{1}/_{2}(C_{45}H_{33}N_{17}O_{14}Th_{2})$	$\begin{array}{c} 31.9\\ 32.5\end{array}$	3.2 2.0	$\begin{array}{c} 13.6 \\ 14.3 \end{array}$		
$Th(NO_3)_4 \cdot 2dipy$ amine	$\rm C_{20}H_{18}N_{10}O_{12}Th$	$\begin{array}{c} 28.8\\ 29.2 \end{array}$	$2.4 \\ 2.2$	$\begin{array}{c} 15.9 \\ 17.0 \end{array}$		
$Th(NO_3)_4 \cdot 2pyrazine \cdot 6 H_2O$	$\mathrm{C_8H_{20}N_8O_{18}Th}$	$\begin{array}{c} 12.1 \\ 12.8 \end{array}$	$2.6 \\ 2.7$	$\begin{array}{c} 14.2 \\ 15.0 \end{array}$		
$Th(NO_3)_4 \cdot 2pipy \cdot 6 H_2O$	$C_{10}H_{34}N_6O_{18}Th$	$\begin{array}{c} 15.0 \\ 15.8 \end{array}$	$3.4 \\ 4.5$	$\begin{array}{c} 10.4 \\ 11.1 \end{array}$		
$Th(NO_3)_4 \cdot 2py N$ -oxide · EtAc	$\rm C_{14}H_{18}N_6O_{16}Th$	$\begin{array}{c} 22.3\\ 22.2 \end{array}$	$\begin{array}{c} 3.8\\ 2.4 \end{array}$	$\begin{array}{c} 10.6\\11.1\end{array}$		
$\text{Th}(\text{NO}_3)_4 \cdot 4\text{picolinic acid} \cdot 4 \text{ H}_2\text{O}$	${\rm C_{24}H_{28}N_8O_{24}Th}$	$\begin{array}{c} 27.4\\ 27.6\end{array}$	$2.9 \\ 2.7$	$\begin{array}{c} 10.3 \\ 10.7 \end{array}$		

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that thorium is ten-coordinated to four bidentate nitrate groups and two oxygen atoms from triphenylphosphine oxide. The structure of this complex provide an example of the ion remaining bidentate even in a sterically crowded situation.

The P=O absorption band in DiPhOS ethane dioxide is reported [8] to be at 1190 cm⁻¹. The spectrum of the complex, $Th(NO_3)_4 \cdot 1.5$ DiPhOS ethane dioxide, shows two strong bands at 1130 and 1080 cm⁻¹ (Fig. 2).







The shift of this band is attributed to coordination through oxygen [5]. The splitting may account for the different mode of coordination of this ligand to thorium(IV) [6].

The stoichiometry of this complex can be explained if bridging takes place as in the proposed structure:



In such complex one of the ligand molecules acts as a bidentate ligand and donation occurs through both oxygen atoms. The coordination number of thorium in this complex is presumably ten.

Similar structure for the adducts obtained with dimethyl acetamide (dma) has been suggested on the basis of the infrared spectrum of the complex [19, 20].

No evidence could be found for the formation of a simple adduct of the type $Tn(NO_3)_4 \cdot DiPhOS$ ethane (or DiPhOS ethane disulphide). This is probably because of the low donor strengths of the phosphorus and sulphur atoms with respect to thorium(IV).

In the spectrum of free pyridine-N-oxide, the frequency of the N-O group occurs at 1180 cm⁻¹. This band shifts to 1310 cm⁻¹, on complexing with thorium nitrate. The ligand in this complex is considered to be coordinated to thorium(IV) through the N-O group (Fig. 3).

Similarly, the C=O stretching band at 1720 cm⁻¹ in free picolinic acid shifts to lower frequencies on complexing with thorium nitrate, whereas the C=N vibration band at 1610 cm⁻¹ is not altered. Thus, it is concluded that picolinic acid is linked to thorium(IV) nitrate through its carboxylic group.



Fig. 3a. The infrared spectrum of pyridine N-oxide



The spectra of the other complexes formed between Th(IV) nitrate and N-donors are too complicated to allow any band assignments. It was not easy to distinguish between the absorption bands of the coordinated ligands and that of the nitrate as they interfere. Similar results have been reported [21].

Thermal Analysis

The thermal stability of the thorium nitrate complexes was investigated over the range 25-800 °C. It was found that these complexes decompose on heating. The molecular weight of the intermediate compounds is calculated from the graphs. The final products after heating up to 800 °C are usually ThO₂ or ThO(NO₃)₂. Table II shows the effect of heat on some thorium nitrate complexes.

Conductivity Measurements

Within the solubility limits of the complexes obtained, the molar conductivities of millimolar solutions at infinite dilution in acetonitrile and

dimethyl formamide have been measured (Table III). The values reported indicated the number and type of ions in solution [22, 23].

As shoon in Table III, the complexes which are soluble in acetonitrile are weak electrolytes.

When dimethylformamide has been used as a solvent, all the adducts which are soluble in this solvent behave as weak electrolytes, except $Th(NO_3)_4 \cdot 2$ -phen $\cdot 2$ EtAc and $Th(NO_3)_4 \cdot 2$ py-N-oxide \cdot EtAc which behave as strong electrolytes. The complex formed between thorium nitrate and picolinic acid, $Th(NO_3)_4 \cdot 4$ -picolinic $\cdot 4 H_2O$ also behaves as a strong electrolyte in dimethylformamide.

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Тетр. (°С)	$M_{\rm obs.}$	Mobs. Formula		
$Th(NO_3)_4 \cdot 1.5$	5 DiPhOS etha	ne dioxide		
$\begin{array}{r} 25-80\\ 120-160\\ 480-800 \end{array}$	$1125.7 \\1075 \\450.3$	Th(NO ₃) ₄ \cdot 1.5 DiPhOS ethane did Th(NO ₃) ₄ \cdot 1.5 Diphos ethane ThO ₂ , Ph ₂ P	(A) (B)	$1125.7 \\ 1077.6 \\ 449$
$Th(NO_3)_4 \cdot 2-C$	o-phen · 2 EtA	c		
$25 - 80 \\ 440 - 800$	$\begin{array}{c} 1016.7\\ 270\end{array}$	$Th(NO_3)_2 \cdot 2$ -o-phen $\cdot 2 EtAc$ ThO_2	(C)	$\begin{array}{c} 1016.7\\ 264\end{array}$
$Th(NO_3)_4 \cdot 2$	DM-o-phen · 4	H_2O		
$\begin{array}{rrr} 25 - & 80 \\ 100 - 140 \\ 320 - 340 \\ 440 - 800 \end{array}$	968.6 926.5 694.9 273.7	$\begin{array}{l} {\rm Th}({\rm NO}_3)_4 \cdot 2 \ {\rm DM}\text{-}o\text{-}{\rm phen} \cdot 4 \ {\rm H}_2{\rm O} \\ {\rm Th}({\rm NO}_3)_4 \cdot 2 \ {\rm DM}\text{-}o\text{-}{\rm phen} \cdot 2 \ {\rm H}_2{\rm O} \\ {\rm Th}({\rm NO}_3)_4 \cdot o\text{-}{\rm phen} \cdot 2 \ {\rm H}_2{\rm O} \\ {\rm Th}{\rm O}_2 \end{array}$	(D) (E) (F)	$968.6 \\ 932.6 \\ 696.2 \\ 264$
$Th(NO_3)_2 \cdot 2$	dipy amine			
$25 - 140 \\ 420 - 800$	$\substack{\textbf{822.46}\\\textbf{310}}$	Th(NO ₃) ₂ · 2dipy amine mix.	(H)	822.46
$Th(NO_3)_4 \cdot 2p$	y N-oxide · E	Ac		
$25 - 200 \\ 300 - 800$	$\begin{array}{c} 758.3 \\ 265.4 \end{array}$	$\begin{array}{l} {\rm Th(NO_3)_4} \cdot {\rm 2py} \ N{\rm -oxide} \ \cdot \ {\rm EtAc} \\ {\rm ThO_2} \end{array}$	(J)	758.3 264
$Th(NO_3)_4 \cdot 4p$	icolinic acid \cdot	$4 H_2 O$		
80 - 100 210 - 240 500 - 800	1044.6-981.9 835.7 376.1	${ m Th(NO_3)_4} \cdot 4 { m picolinic} \ { m acid} { m Th(NO_3)_4} \cdot 3 \ { m picolinic} \ { m acid} { m ThO(NO_3)_2}$	(K) (L)	972.6 849.33 372
$Th(NO_3)_4 \cdot 2_1$	$pipy \cdot 6 H_2O$			
25 - 80 460 - 800	758 485	Th(NO ₃) ₄ · 2pipy · 6 H ₂ O Th(NO ₃) ₄		758.4 480

Thermal decomposition of some thorium nitrate complexes

Where $M_{\rm obs.}$ – observed molecular weight, $M_{\rm cal.}$ – calculated molecular weight The letters indicate intermediate stages

Tab	le l	П
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Conductivities of some thorium nitrate complexes in different solvents

	A ohn	1^{-1} cm ²	
Compound	MeCN	DMF	
$Th(NO_3)_4 \cdot 1.5 DiPhOS$ ethane dioxide	W	_	
$Th(NO_3)_4 \cdot 2(o-phen) \cdot 2 EtAc$	<u> </u>	65	
Th(NO ₃) ₄ · 1.5(2,2',2"-tripy)	W		
$Th(NO_3)_4 \cdot 2.bipy \cdot 4 H_2O$	-	W	
$Th(NO_3)_4 \cdot 1.5 DM$ -bipy	_	W	
$Th(NO_3)_4 \cdot 2$ -dipy amine	-	W	
Th(NO ₃) ₄ · 2(py N-oxide) · EtAc	_	73	
$Th(NO_3)_4 \cdot 4(picolinic acid) \cdot 4 H_2O$	-	136	
		5.2	

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0.0-DIETHYLPHOSPHONOTHIOYL DITHIOCARBAMATE DERIVATIVES OF SOME ORGANO-TITANIUM(IV), -ZIRCONIUM(IV) AND -OXOMOLYBDENUM(VI) COMPOUNDS*

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A number of 0,0-diethylphosphonothioyl dithiocarbamate derivatives of the type $(\eta^5-R)_2M\{S_2CNHPS(OEt)_2\}CI$ [R = C_5H_5 , $CH_3C_5H_4$, C_9H_7 ; M = Ti(IV), Zr(IV) and OMo(VI)] have been synthesised and characterised on the basis of elemental analyses, magnetic measurements, electrical conductance and spectral studies (IR, NMR, UV and visible).

Introduction

Potassium 0,0-diethylhposphonothioyl dithiocarbamate is useful for the preparation of certain insecticidal heterocyclic compounds [1]. Beside its biological significance, the 0,0-diethylphosphonothioyl dithiocarbamate ligand has a structural importance, too. It can form either monodentate or bidentate metal complexes. Our interest in the investigation of the bonding mode of various dithiocarbamate ligands [2-5], prompted us to synthesise a few complexes of 0,0-diethylphosphonothioyl dithiocarbamate of the type $(\eta^5-R)_{2}M\{S_{2}CNHPS(OEt)_{2}\}Cl \ [R = cyclopentadienyl (C_{5}H_{5}), methylcyclopen$ tadienyl (CH₃C₅H₄), indenyl (C₉H₇); M = Ti(IV), Zr(IV) and OMo(VI)]. IR and UV spectral studies demonstrate that in these complexes the dithiocarbamate group is bidentate similar to those reported earlier [2-5]. Conductivity measurements in nitrobenzene solution indicate that these complexes are non--electrolytes. The complexes are fairly stable in inert atmosphere but decompose on standing in air.

Results and Discussion

The preparation of the complexes may be represented by the following general equation:

$$(\eta^5-R)_2MCl_2 + (EtO)_2PSNHCS_2^-K^+ \rightarrow (\eta^5-R)_2M\{S_2CNHPS(OEt)_2\}Cl + KCl$$

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All the complexes are soluble in acetone, DMSO, THF and partly soluble in halogenated hydrocarbons. These are kinetically reactive and decompose on standing in air. Magnetic susceptibility values at room temperature show that all compounds are diamagnetic. The molar conductance of $10^{-3} M$ solution of these complexes in nitrobenzene were found to be of the order of 0.5 ohm⁻¹ cm² mole⁻¹. These conductivity results indicate the covalent nature of the compounds and the absence of ionic species in solution. Table I lists the analytical data and some physical characteristics of the complexes.

Compound	Colour	Dec.	Conductiv- Dec. ity Data Temp. (%) Found (Calc.)		
	Colour	°C	$\frac{\text{molarity} \times}{10^3 = 0.3}$	М	S	N		
$(\eta^5$ -C ₅ H ₅) ₂ Ti(DPD)Cl	Yellow	208	0.52	10.56 (10.47)	20.86 (20.98)	7.86 (7.76)	3.12 (3.06)	
$(\eta^5$ -CH ₃ C ₅ H ₄) ₂ Ti(DPD)Cl	Pale yellow	192	0.50	9.93 (9.86)	19.85 (19.77)	7.40 (7.31)	2.79 (2.88)	
$(\eta^5$ -C ₉ H ₇) ₂ Ti(DPD)Cl	Yellow	176	0.52	8.64 (8.59)	17.30 (17.22)	6.43 (6.36)	2.59 (2.51)	
$(\eta^5$ -C ₅ H ₅) ₂ Zr(DPD)Cl	Pale yellow	136	0.51		19.25 (19.17)	7.17 (7.08)	2.85 (2.79)	
$(\eta^5$ -CH $_3$ C $_5$ H $_4)_2$ Zr(DPD)Cl	Pale yellow	131	0.54	17.33 (17.25)	18.24 (18.15)	6.65 (6.71)	2.58 (2.64)	
$(\eta^5 - C_9 H_7)_2 Zr(DPD)Cl$	Light brown	102	0.53	15.26 (15.18)	15.89 (15.98)	5.81 (5.90)	2.40 (2.33)	
$(\eta^5$ -C ₅ H ₅) ₂ MoO(DPD)Cl	Brown	198	0.50	18.90 (18.98)	18.89 (18.98)	7.11 (7.02)	2.83 (2.76)	
$(\eta^5$ -CH ₃ C ₅ H ₄) ₂ MoO(DPD)Cl	Brown	192	0.52	17.88 (17.98)	17.90 (17.99)	6.72 (6.65)	2.70 (2.62)	
$(\eta^5$ -C ₉ H ₇) ₂ MoO(DPD)Cl	Brown	168	0.51	15.92 (15.84)	15.76 (15.85)	5.95 (5.86)	2.39 (2.31)	

Table I							
nalytical	data	and	physical	characteristics			

(DPD): 0,0-diethylphosphonothioyl dithiocarbamate $^{(a)}$ in ohm⁻¹ cm² mole⁻¹

A

Whether the dithiocarbamate group is monodentate or bidentate, is reflected in the $v(C \\displaystyle S)$ stretching frequency. The presence of only one strong band in the $\sim 1000 \ \mathrm{cm}^{-1}$ region, supports a bidentate behaviour of the dithiocarbamates, a doublet being expected in the $1000 \\pm 50 \ \mathrm{cm}^{-1}$ in the monodentate behaviour [6-8]. Hence from a structural viewpoint, IR spectroscopy serves to distinguish between a monodentate and bidentate dithiocarbamate group. All the complexes, reported in this communication possess only one medium absorption band at $\sim 1000 \ \mathrm{cm}^{-1}$ which supports the biden-

tate nature of the dithiocarbamate ligand and also suggests that the ligand is chelating in all the cases.

The band around 1370 cm⁻¹ is assigned to the $v(C \cdots N)$ stretching frequency. The occurrence of this band at lower energy as compared with those of the corresponding dialkyldithiocarbamate complexes [4] indicates considerably less double bond character of the $(C \cdots N)$ bond in these complexes. The presence of ethoxy groups in the dithiocarbamate moiety considerably weakens the drift of electrons towards the sulphur atoms due to strong electron withdrawing mesomeric effect and therefore the double bond formation of the $(C \cdots N)$ bond is considerably less in O,O-diethylphosphonothioyl dithiocarbamate complexes, as compared to those of dialkyldithiocarbamates.

Absorptions owing to the P=S stretching vibrations occur at \sim 750 cm⁻¹. The free ligand shows this absorption at \sim 760 cm⁻¹. Since there is no significant shift of ν (P=S) in the complexes, as compared to the ligand, it is unlikely that the atom attached directly to the phosphorus could act as a coordinating centre.

The strong absorptions at ~1110 cm⁻¹ are characteristic of the C-O stretching vibration in C₂H₅OP group, while that at \sim 3075 cm⁻¹ are due to the N-H stretching frequencies. The medium intensity bands in the range 365-345 cm⁻¹ are assigned to the metal sulphur vibrational frequencies [9]. The presence of Mo=O group in molybdenum derivatives is confirmed by the appearance of a sharp absorption band at \sim 900 cm⁻¹. The relevant IR data are depicted in Table II.

Compound	ν(M—S)	ν(M—Cl)	ν(CN)	ν(CS)	ν(F=S)	ν(CP)
$(\eta^5$ -C ₅ H ₅) ₂ Ti(DPD)Cl	355 (m)	375 (m)	1375 (s)	1005 (s)	755 (m)	1125 (s)
$(\eta^{5}\text{-}\mathrm{CH}_{3}\mathrm{C}_{5}\mathrm{H}_{4})_{2}\mathrm{Ti}(\mathrm{DPD})\mathrm{Cl}$	365 (m)	370 (m)	1380 (s)	1015 (s)	745 (m)	1120 (s)
$(\eta^5 - C_9 H_7)_2 Ti(DPD)Cl$	360 (m)	375 (m)	1370 (s)	995 (s)	750 (m)	1105 (s)
$(\eta^5$ -C ₅ H ₅) ₂ Zr(DPD)Cl	345 (m)	380 (m)	1375 (s)	1005 (s)	750 (m)	1115 (s)
$(\eta^5$ -CH ₃ C ₅ H ₄) ₂ Zr(DPD)Cl	350 (m)	370 (m)	1360 (s)	1000 (s)	755 (m)	1110 (s)
$(\eta^5 - C_9 H_7)_2 Zr(DPD)Cl$	345 (m)	380 (m)	1365 (s)	990 (s)	760 (m)	1105 (s)
$(\eta^5 - C_5 H_5)_2 MoO(DPD)Cl$	360 (m)	375 (m)	1360 (s)	1010 (s)	755 (m)	1105 (s)
$(\eta^5\text{-}\mathrm{CH}_3\mathrm{C}_5\mathrm{H}_4)_2\mathrm{MoO(DPD)Cl}$	355 (m)	385 (m)	1375 (s)	1000 (s)	745 (m)	1120 (s)
$(\eta^5 - C_9 H_7)_2 MoO(DPD)Cl$	350 (m)	385 (m)	1370 (s)	995 (s)	750 (m)	1125 (s)

	Table .	п	
Relevant	infrared	data	(cm^{-1})

(s) = strong; (m) = medium

The NMR spectra of the complexes are simple and easily interpreted. The intensities were determined by planimetric integration of these spectra

and the integrated proton ratios correspond to the formula

 $(\eta^{5}-R)_{2}M\{S_{2}CNHPS(OEt)_{2}\}Cl.$

Although the ethoxy protons are distant from the sulphur atoms, their resonance signals are shifted to a lower field as compared to the free ligand. The signals of NMR spectra are sharp, without being split indicating the non-coexistence of mono and bidentate dithiocarbamate groups in the complexes. This fact, however, does not imply directly that the two thiocarbamates are bonded equivalently since the protons are at a considerable distance from the metal-sulphur bonds [10]. Nevertheless, the spectra show no trace of free ligand indicating that the chelates do not dissociate upon dissolution in acetone. Whereas the resonance due to C_5H_5 protons occur as a sharp singlet, that due to the C_5H_4 protons of η^5 -CH₃C₅H₄ observed as a comparatively broad peak. The NMR data are listed in Table III.

The electronic spectra of the complexes, exhibit a single band in the 24 700-24 350 cm⁻¹ region which may be assigned to the charge transfer band [11, 12] in accordance with the electronic configuration $(n-1)d^{\circ}ns^{\circ}$ of the metal ion in each case. The diamagnetic dithiocarbamates are of particular interest since they do not absorb in much of the visible region of the spectrum. Hence the absorption in the UV region arising as a result of the internal tran-

Compound	R	—NH	—POCH ₂ —	—CH3
$(\eta^5 - C_5 H_5)_2 Ti(DPD)Cl$	$\mathrm{R}=\mathrm{C}_{5}\mathrm{H}_{5}$ 6.0 (s)	4.82	4.18 (m)	1.35 (t) J = 7.0 Hz
$(\eta^{5}\text{-}\mathrm{CH}_{3}\mathrm{C}_{5}\mathrm{H}_{4})_{2}\mathrm{Ti}(\mathrm{DPD})\mathrm{Cl}$	$R = CH_3C_5H_4$ 5.8 (s), 2.22 (s)	4.83	4.22 (m)	1.32 (t) J = 7.2 Hz
$(\eta^5$ -C ₉ H ₇) ₂ Ti(DPD)Cl	$R = C_9 H_7$ 6.80 - 7.25 (m)	4.85	4.21 (m)	1.34 (t) J = 7.1 Hz
$(\eta^5$ -C ₅ H ₅) ₂ Zr(DPD)Cl	$\begin{array}{l} \mathbf{R}=\mathbf{C}_{5}\mathbf{H}_{5}\\ 5.98\ (\mathbf{s})\end{array}$	4.80	4.17 (m)	1.36 (t) J = 6.8 Hz
$(\eta^5\text{-}\mathrm{CH}_3\mathrm{C}_5\mathrm{H}_4)_2\mathrm{Zr}(\mathrm{DPD})\mathrm{Cl}$	$R = CH_3C_5H_4$ 5.85 (s), 2.20 (s)	4.82	4.23 (m)	$egin{array}{c} 1.33\ J=7.0{ m Hz} \end{array}$
$(\eta^5$ -C ₉ H ₇) ₂ Zr(DPD)Cl	$R = C_9 H_7$ 6.82-7.32 (m)	4.80	4.18 (m)	$egin{array}{c} 1.30\ J=7.1 \ { m Hz} \end{array}$
$(\eta^5$ -C ₅ H ₅) ₂ MoO(DPD)Cl	$\begin{array}{l} \mathbf{R}=\mathbf{C}_{5}\mathbf{H}_{5}\\ 6.08\ \mathbf{(s)}\end{array}$	4.83	4.22 (m)	$egin{array}{c} 1.31\ J=7.0{ m Hz} \end{array}$
$(\eta^{5}\text{-}\mathrm{CH}_{3}\mathrm{C}_{5}\mathrm{H}_{4})_{2}\mathrm{MoO(DPD)Cl}$	${f R}={f C}{f H}_{3}{f C}_{5}{f H}_{4}$ 5.82 (s), 2.21 (s)	4.85	4.17 (m)	$egin{array}{c} 1.34\ J=6.8~{ m Hz} \end{array}$
$(\eta^5$ -C ₉ H ₇) ₂ MoO(DPD)Cl	$R = C_9 H_7$ 6.80-7.22 (m)	4.82	4.20 (m)	$egin{array}{c} 1.32\ J=7.2{ m Hz} \end{array}$

Table III

Proton chemical shifts (δ) and coupling constant data

sitions among the chromophore groups present in the ligand can be studied. All the complexes show an intense band at $\sim 35\ 000\ \mathrm{cm}^{-1}$ arising due to the $\pi \to \pi^*$ transitions of the N····C····S group [13, 14]. The position of this band is shifted to a lower energy due to the electron withdrawing ability of the amine group in the ligand. Another band which is expected to occur at $\sim 30\ 000\ \mathrm{cm}^{-1}$ due to the $\pi \to \pi^*$ transition in the S····C···S group, and is associated with the equivalence of the C–S bonds, is not observed as a prominent band in these complexes, showing that the dithiocarbamate ligand is bidentate. This fact is also confirmed by IR spectroscopy.

Experimental

The metal contents, nitrogen and sulphur were estimated by standard methods [15]. Nitrobenzene was purified for conductance measurements by the method described by FAY et al. [16]. Various transition metal derivatives, $(\eta^5 \cdot R)_2 TiCl_2$ [17–19], $(\eta^5 \cdot R)_2 ZrCl_2$ [19–21] and $(\eta^5 \cdot R)_2 MoOCl_2$ [22], $(R = C_5H_5, CH_3C_5H_4$ and C_5H_7) were prepared by standard methods. Potassium O,O-diethylphosphonothioyl dithiocarbamate was prepared by the method described by ADDOR [1].

Conductance measurements were made in nitrobenzene at 30.00 ± 0.05 °C using a Beckmann Conductivity Bridge (Model R. C. 18A). In the magnetic measurements mercury tetrathiocyanatocobaltate(II) was used as a calibrant. Solid state IR spectra were recorded in KBr pellets in the $4000-200 \text{ cm}^{-1}$ region on a Perkin-Elmer 621 grating spectrophotometer. Visible and UV spectra were recorded on a CØ Russian recording spectrophotometer and Beckmann DU-2 spectrophotometer. ¹H NMR spectra were recorded at a sweep width of 900 Hz with a Perkin-Elmer R-32 spectrophotometer. Chemical shifts are expressed relative to an internal reference to TMS (1% by volume).

Preparation of complexes

Potassium salt of O,O-diethylphosphonothioyl dithiocarbamate was refluxed separately with equimolar quantities of transition metal complexes of the type $(\eta^5\text{-R})_2\text{MCl}_2$ [R = $C_5\text{H}_5$, CH₃C₅H₄, C₉H₇; M = Ti(IV), Zr(IV) and OMo(VI)] in dichloromethane for about 10 hrs. The hot solution was filtered through a G-4 sintered glass disk. The filtrate was concentrated under vacuum. The products were obtained by adding petroleum ether (60-80 °C) to the concentrated filtrate and allowing the mixture to stand overnight.

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THE SYNTHESIS OF SOME COMPLEX QUINAZOLINE DERIVATIVES CONTAINING ONE OR TWO QUINAZOLINE RINGS AND CARRYING AMINO, ACYLAMINO, ESTER AND/OR CARBAMATE FUNCTIONAL GROUPS IN THEIR SIDE CHAINS

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The scope of the Bischler synthesis has been extended to the synthesis of the complex quinazoline derivatives 3b-3d, 5a-5f, 6a, 6b, 7 and 8. Reductive cleavage of the C-N bond of all 4-(*N*-monosubstituted aminomethyl)quinazolines tested took place on treatment with ethanol in the presence of acids or bases.

Recently the photolysis [1] and thermolysis [2] of ethyl N-(2-methyl--4-methylene-6,7-methylenedioxy-3,4-dihydro-3-quinazolinyl)-N-phenylcarbamate (1) have been studied. In connection with the structure elucidation of three characteristic products of these reactions, viz. ethyl N-(2-methyl-6,7--methylenedioxy-4-quinazolinylmethyl)-N-phenylcarbamate (2a) [1, 2], ethyl N--[2-(2-methyl-6,7-methylenedioxy-4-quinazolinylmethyl)phenyl]-carbamate(3a) [1, 2] and ethyl N-[1,2-bis(2-methyl-6,7-methylenedioxyquinazolinyl)ethyl]--carbamate (4) [2], attempts to synthesize some isomers of these compounds were undertaken. Here we wish to report on the syntheses of the isomers 3b, 5a** and 6a of 2a and 3a, as well as of the isomers 7 and 8 of 4.

The key-step of all (successful and unsuccessful) syntheses was the Bischler cyclization [3, 4] (Scheme 1) of the appropriate 2'-acylanilides (9d, 10a-10d, 11b, 12c and 13c) by heating with ethanolic ammonia in sealed tubes. With the exception of compound 10a which contains a free NH group α to the keto group, all other 2'-acylanilides tested furnished the corresponding



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** 5a could, in principle, have been formed by a photo-Fries type rearrangement of 2a.



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quinazolines (3d, 5b-5d, 6b, 7 and 8, respectively) in 31-78% yields. These cyclizations are extensions for the preparation of functionalized quinazoline derivatives of the Bischler quinazoline synthesis [3, 4].

Some by-products were formed in the ring closures of the type 10 compounds. In the **b** series they were identified as 5a, ethyl 4-aminobenzoate, and, probably, 10a, *i.e.* the *N*-deformylation products of the starting compound (10b) and of its cyclization product (5b), respectively. Ethyl 4-aminobenzoate was the only identified product (85% yield) of the attempted Bischler cyclization of 10a; considerable amounts of tars were formed in addition.

Successive N-deacetylation of 3d and N-ethoxycarbonylation of the resulting 3c completed the synthesis of the quinazoline 3b, and N-ethoxy-carbonylation of 6b furnished 6a. The N-deacylations of compounds 5b-5d, on the other hand, presented difficulties. Both the base- and acid-catalyzed alcoholyses (or hydrolyses) led to complex mixtures with ethyl 4-aminobenzoate being the main product in several cases. 2,4-Dimethyl-6,7-methylenedioxy-quinazoline was also obtained in some cases;* the formation of these two products is apparently the result of reductive cleavage of the 4-CH₂-N
bond of the starting compounds; the nature of this process is not clear. In some cases (see Experimental) the desired N-deacylated product 5a was formed in addition to the product of hydrolysis of the ester group (5e and 5f). Attempted hydrogenolysis and decarboxylation of compound 5d to obtain 5a failed, probably because of concomitant hydrogen addition to the nitrogen-containing ring (cf. Ref. [7]).

The intermediate 2'-acylanilides were obtained by straightforward methods. Thus, nitration of compound 9a furnished 9b which was reduced and acetylated to obtain 9d. Compound 11d, obtained by treating 2'-acetyl-4',5'--methylenedioxyacetanilide [2] with bromine in dichloromethane, was allowed to react with ethyl 4-aminobenzoate and the resulting 10a was N-acylated with acetic formic anhydride, acetic anhydride and benzyl chloroformate, respectively, to obtain compounds 10b-10d. A by-product of the acetylation of compound 10a was compound 14 which, under appropriate conditions (see Experimental) became the main product. Compound 14 was also formed on refluxing 10c with excess acetic anhydride. When heated with ethanolic ammonia, it furnished 5c. Treatment of compound 11a with aniline and benzylamine, respectively, furnished 11b and 11c. The latter was allowed to react with 11d to obtain 12a, which was successively N-debenzylated and N-ethoxycarbonylated to yield compound 12c via 12b. When allowed to react with benzylamine (0.5 mol for 1 mol of 11d), 11d furnished 13a which was similarly converted into 13c via 13b.

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^{*} Similarly, the acid-catalyzed reaction of ethyl N-(2-methyl-6,7-methylenedioxy-4--quinazolinylmethyl) carbamate (2b) with ethanol led to the formation of 2,4-dimethyl-6,7--methylenedioxyquinazoline and ethyl carbamate.

Experimental

IR and UV spectra were recorded with Hungarian Optical Works (Budapest) Type Spektromom and Unicam Type SP 700 spectrometers, respectively. The ¹H-NMR spectra were obtained, except where noted, at 60 MHz in CDCl_3 solution on a Perkin-Elmer Type R 12 spectrometer with TMS as internal reference. The mass spectra were obtained on a Varian MAT 311A (Grant No. 511-3809 from the Danish Natural Science Research Council) by electron impact (70 eV) and using direct insertion.

3',4'-Methylenedioxy-2-(4-nitrophenyl)acetophenone (9a)

AlCl₃ (6.6 g; 50 mmol) was added at -35 °C to a mixture of 1,3-benzodioxole (6.1 g; 50 mmol), *p*-nitrophenylacetyl chloride (10.0 g; 50 mmol) and dichloromethane (50 mL) with continuous stirring. Stirring was continued at this temperature for 3 h, and the resulting purple mixture was poured into water (50 mL). The organic layer was washed with water, 5% aqueous NaOH and water, dried (MgSO₄) and evaporated to dryness. The residue was crystallized from ethanol to obtain 7.2 g (51%) of compound **9a**, m.p. 143 °C.

C15H11NO5 (285.25). Calcd. N 4.91. Found N 4.95%.

IR (KBr): 1670 cm⁻¹.

4',5'-Methylenedioxy-2'-nitro-2-(4-nitrophenyl)acetophenone (9b)

A mixture of compound 9a (1.45 g; 5 mmol) and conc. HNO₃ (d 1.41; 20 mL) was stirred for 30 min at 20 °C and then poured onto ice (30 g). The resulting crystalline product was washed with water and recrystallized from BuOH to obtain 1.52 g (92%) of compound 9b, m.p. 190 °C.

 $C_{15}H_{10}N_{2}O_{7}$ (330.25). Calcd. C 54.35, H 3.05, N 8.64. Found C 54.55, H 3.05, N 8.48%. IR (KBr): 1710 cm^{-1}.

2'-(Acetylamino)-2-(4-acetylaminophenyl)-4',5'-methylenedioxyacetophenone (9d)

A suspension of compound **9b** (0.95 g; 2.9 mmol) in ethyl acetate (100 mL) was reduced in the presence of an 8% Pd/C catalyst (1.0 g) at ordinary pressure and room temperature. After the uptake of the calculated amount of hydrogen, the catalyst was filtered off and the filtrate evaporated to dryness. The crude **9c** was taken up in dichloromethane (10 mL) and the resulting suspension stirred with acetic anhydride (1 mL) until a clear solution was formed from which precipitation of the colourless crystals of the title compound **9d** soon started. The product (0.65 g; 63.9%; m.p. 267-269 °C) was filtered off and washed with ether.

 $C_9H_{16}N_2O_5$ (354.35). Calcd. C 64.40; H 5.12, N 7.91. Found C 64.41, H 5.22, N 7.85%. IR (KBr): 3250, 3100, 1690, 1660 and 1640 cm⁻¹.

Ethyl 4-[(2'-acetylamino-4',5'-methylenedioxyphenacyl)amino]benzoate (10a)

A mixture of compound 11d (see below) (1.5 g; 5 mmol), ethyl 4-aminobenzoate (5.0 g; 30 mmol) and EtOH (50 mL) was refluxed for 3 h. The mixture remained heterogeneous throughout. After cooling, the crude product was filtered off and recrystallized from DMF to yield 1.0 g (54%) of pure 10a, m.p. 259-260 °C.

 $\rm C_{20}H_{20}N_{2}O_{6}$ (384.48). Calcd. C 62.49, H 5.24, N 7.29. Found C 62.71, H 5.37, N 7.28%. IR (KBr): 3450, 3200, 1730, 1700 and 1650 cm^{-1}.

N-Formylation of compound 10a

Compound 10a (2.0 g) was refluxed with acetic formic anhydride (10 mL). The mixture, was evaporated to dryness. When triturated with ether, the oily residue turned crystalline. Recrystallization from EtOH furnished 83% of compound 10b, m.p. 169 °C.

 $C_{21}H_{20}N_2O_7$ (412.39). Calcd. C 61.16, H 4.89, N 6.79. Found C 61.06, H 4.78, N 6.95%. IR (KBr): 1720 b, 1695 and 1650 cm⁻¹.

¹H-NMR: δ 1.40t + 4.35q, COOEt; 2.15s, Ac; 5.1s, COCH₂N; 5.95s, OCH₂O; 7.2s, 3'-H; 7.15 + 8.05, AA'BB' spectrum, $J_{gem} = 8.5$ Hz, ArH's of *p*-disubstituted benzene ring; 8.35s, 6'-H; 8.65s, formyl-H.

Reaction of compound 10a with acetic anhydride

(a) A mixture of compound 10a (3.84 g; 10 mmol), acetic anhydride (2.0 g; 20 mmol) and dry dioxane (80 mL) was refluxed for 11 h. During this period the original suspension gradually turned into a clear solution which was then evaporated to dryness in vacuum. The oily brown residue was triturated with ether to obtain 3.67 g (86%) of the crystalline compound 10c, m.p. 170-172 °C (from EtOH).

 $C_{22}H_{22}N_2O_7$ (426.42). Calcd. C 61.96, H 5.20, N 6.57. Found C 62.06, H 5.49, N 6.37%. IR (KBr): 3250, 1730, 1700 and 1670 cm⁻¹, b.

¹H-NMR: δ 1.4t + 4.4q, CODEt; 2.0s and 2.2s, two Ac groups; 5.0s, COCH₂N; 6.0s, OCH₂O; 7.1s, 3'-H; 7.4 + 8.1, AA'BB' spectrum, $J_{\text{gem}} = 8.5$ Hz, ArH's of *p*-disubstituted benzene ring; 8.35s, 6'-H.

(b) A mixture of compound 10a (7.7 g; 20 mmol) and acetic anhydride (53 mL) was refluxed for 2 h and evaporated to dryness in vacuum. The resulting brown oil was taken up in ether and allowed to stand for several days in a refrigerator to obtain crude 14 as a yellow solid (4.9 g, m.p. 142-150 °C), which after recrystallization from EtOH furnished 1.9 g (23%) of pure 14, m.p. 142-143 °C.

C22H20N2O6 (408.41). Calcd. N 6.86. Found N 6.80%.

IR (KBr): 1705, 1665 and 1595 cm⁻¹.

¹H-NMR: δ 1.38t + 4.35q, J = 7.1 Hz, COOEt; 1.87s, C-Me; 2.12s, Ac; 5.94s, OCH₂O; 6.36 bs, =CH-; 6.46s and 6.82s, 5-H and 8-H; 7.35 + 8.02, AA'BB' spectrum, ArH's of *p*-disubstituted benzene ring.

MS (165 °C), m/z (rel. int.): 408 (M^+ , 100), 366 (50), 365 (87), 363 (8), 337 (30), 309 (37), 292 (8), 264 (6), 263 (5), 243 (3.2), 206 (4.3), 191 (92), 190 (47).

When the filtrate of crude 14 was concentrated and allowed to stand for several days, 1.2 g (14%) of crude 10c was obtained.

(c) A mixture of compound 10c (4.26 g; 10 mmol) and acetic anhydride (30 mL) was refluxed for 2 h (whereby the colour of the solution gradually turned from yellow to red) and allowed to stand overnight. Evaporation of the solvent furnished an oily product which was taken up in ether (25 mL). From the resulting solution compound 14 soon started to precipitate in crystalline form. The product (2.40 g; 69%) was collected next morning and proved identical (IR) with the product obtained according to (b). The filtrate of compound 14 deposited, after standing for a fortnight, 0.62 g (14.5%) of unchanged starting compound.

N-Benzyloxycarbonylation of compound 10a

A mixture of compound **10a** (3.8 g; 10 mmol), anhydrous dioxane (150 mL) and benzyl chloroformate (50 mL) was refluxed until, according to TLC (Kieselgel $PF_{254+366}$; benzene-acetone, 10:1) the starting **10a** had been used up completely (about 1 h), and poured onto ice (200 g). The resulting emulsion was made alkaline with 5% aqueous NaOH and extracted with CH_2Cl_2 . The oily residue, obtained by usual work-up of the organic phase, turned crystal-line when triturated with light petroleum to yield 5.1 g (98%) of compound **10d**, m.p. 172–173 °C which, after being washed with ether, proved homogeneous (TLC).

C₂₈H₂₆N₂O₈ (518.51). Calcd. C 64.85, H 5.05, N 5.40. Found C 64.74, H 5.02, N 5.27%. IR (KBr): 3250, 1720, 1705 and 1665 cm⁻¹.

¹H-NMR: δ 1.35t + 4.3 q, COOEt; 2.15s, Ac; 4.9s and 5.1s, COCH₂N and benzyl methylene; 5.95s, OCH₂O; 7.15 + 7.90 AA'BB' spectrum, $J_{\text{gem}} = 8.5$ Hz, ArH's of *p*-disubstituted benzene ring; 7.2s, 6H, Ph + 3'-H; 8.3s, 6'-H.

2'-Acetyl-2-chloro-4',5'-methylenedioxyacetanilide (11a)

Chloroacetyl chloride (12 mL; 0.15 mol) was added, with stirring and ice-cooling, to a suspension of 2'-amino-4',5'-methylenedioxyacetophenone [2] (17.9 g; 0.1 mol) and Na_2CO_3 (8.0 g; 76 mmol) in dichloromethane (200 mL). The mixture was stirred for 30 min at room temperature. The colourless crystalline product was filtered off, thoroughly washed with

water and then successively with small amounts of methanol and ether to obtain 23.5 g (92%) of the N-chloroacetyl derivative IIa, m.p. 176-177 °C (EtOH).

C₁₁H₁₀CINO₄ (255.66). Calcd. Cl 13.87, N 5.48. Found Cl 13.60; N 5.24%.

IR (KBr): 1680 and 1650 cm⁻¹.

2'-Acetyl-2-anilino-4',5'-methylenedioxyacetanilide (11b)

A mixture of compound 11a (1.27 g; 5 mmol), aniline (7 mL) and anhydrous EtOH (35 mL) was refluxed for 15 h. The product (0.87 g; 54%) separated from the resulting dark solution in the form of colourless needles, m.p. 168 °C.

C17H16N2O4 (312.32). Calcd. C 65.37, H 5.16, N 8.97. Found C 65.45, H 5.38, N 9.22%. IR (KBr): 3350, 1675 and 1650 cm⁻¹.

2'-Acetyl-2-benzylamino-4',5'-methylenedioxyacetanilide (11c)

A mixture of compound 11a (25.6 g; 0.1 mol), acetonitrile (350 mL) and benzylamine (27 mL; 0.25 mol) was refluxed for 3 h. The crystals of benzylammonium chloride soon started to precipitate from the resulting clear solution. The mixture was allowed to cool, the salt was filtered off and the filtrate evaporated to dryness in vacuum. The oily residue was triturated with water to obtain 19.6 g (60%) of compound **11c**, m.p. 118 °C (EtOH). $C_{18}H_{18}N_2O_4$ (326.35). Caled. C 66.24, H 5.56, N 8.59. Found C 66.16, H. 5.67, N 8.76%.

IR (KBr): 3200 and 1640 cm⁻¹.

¹H-NMR: δ 2.58s, Ac; 3.45s, COCH₂N; 3.88s, NCH₂Ph; 6.00s, OCH₂O; 7.15-7.60m, 6 H, Ph + 6'-H; 8.48s, 3'-H.

2'-Bromoacetyl-4',5'-methylenedioxyacetanilide (11d)

Bromine (0.54 mL; 10.5 mmol) was added to a solution of 2'-acetyl-4',5'-methylenedioxyacetanilide [2] (2.2 g; 10 mmol) in CH.Cl. (30 mL), and the mixture was stirred for 10 h at room temperature. The brown colour gradually faded and a colourless product deposited. The latter was filtered off and washed with EtOH (whereupon it turned yellow) to obtain 2.1 g (70%) of compound 11d, m.p. 187 °C (remaining unchanged on recrystallization from dioxane).

Ć11H10BrNO4 (300.12). Calcd. C 44.02, H 3.36, N 4.67. Found C 43.87, H 3.35, N 4.46%. IR (KBr): 3250, 1720 and 1660 cm⁻¹.

Preparation of compound 12a

A solution of compound 11c (3.26 g; 10 mmol) in acetonitrile (100 mL) was treated with compound 11a (3.00 g; 10 mmol) and Na_2CO_3 (3.00 g; 28 mmol). The resulting suspension was refluxed for 3 h with stirring and allowed to cool. The light yellow crystalline product was filtered off, washed successively with acetonitrile, water, methanol and ether to obtain 3.93 g (72%) of compound 12a, m.p. 185-187 °C. Since, according to the ¹H-NMR spectrum, the crude product was sufficiently pure, it was subjected to debenzylation (see below) without further purification.

IR (KBr): 3100, 1675 and 1630 cm⁻¹.

¹H-NMR (CDCl₃ + D₂O): δ 2.23s, Ac-N; 2.57s, Ac-Ar; 3.58s, N-CO-CH₂-N; 4.02s and 4.05s, Ar-CO-CH₂-N and N-CH₂-Ar'; 5.95s + 6.00s, two OCH₂O groups; 7.0-7.7m, 7H, Ph + two ArH's ortho to the two acylamino groups; 8.32s and 8.38s, two ArH's ortho to the two acyl groups.

Debenzylation

Compound 12a (5.46 g; 10 mmol) was hydrogenolyzed in dioxane solution (50 mL) in the presence of an 8% Pd-C catalyst at ambient temperature. After the uptake of the calculated amount of hydrogen, the mixture was heated to its boiling point, the catalyst was removed by filtration from the hot solution and washed with dioxane. The combined filtrate and washings were concentrated to a small volume and allowed to cool to obtain 3.0 g (66%) of compound 12b as yellow crystals, m.p. 215 °C (DMF).

 $C_{22}H_{21}N_3O_8$ (455.41). Calcd. C 58.02, H 4.65, N 9.23. Found C 57.83, H 4.69, N 9.13%. IR (KBr): 3070, 1680 and 1635 cm^{-1}.

¹H-NMR (DMSO- d_6 ; reference DMSO- $d_5 = 2.50$): δ 2.10s, Ac-N; ~2.5s, Ac-Ar, merged with the reference signal; 3.28s and 3.37s, N-CO-CH₂-N and HDO; 4.10s, Ar-CO-CH₂-N; 6.08s, 4H, two OCH₂O groups; 7.45s, 7.50s, 7.97s and 8.24s, four ArH's.

Ethoxycarbonylation

A suspension of compound 12b (2.3 g; 5 mmol) in anhydrous dioxane (200 mL) was treated with ethyl chloroformate (1.2 mL; 13 mmol) and refluxed with continuous stirring whereby a clear solution was gradually formed. After about 20 min another portion of ethyl chloroformate (1.2 mL) and pyridine (0.8 mL; 10 mmol) were added. The mixture was refluxed for further 30 min, treated with charcoal and poured onto ice. The resulting aqueous solution was extracted with dichloromethane. The oil residue, obtained after conventional work-up of the dichloromethane solution, was triturated with light petroleum to obtain 1.98 g (75%) of compound 12c, m.p. 151-152 °C. Since, according to its ¹H-NMR spectrum, the crude product was sufficiently pure, it was subjected to ring closure (see below) without further purification.

IR (KBr): 1695 and 1640 cm⁻¹.

¹H-NMR: δ 1.24t + 4.24 q, J = 7 Hz, COOEt; 2.20s, Ac-N; 2.56s, Ac-Ar; 4.15s, N-CO-CH₂-N; 4.80 bs (or possibly the very close inner peaks of an AB spectrum), Ar-CO-CH₂; 6.00s, 4H, two OCH₂O groups; 7.15s and 7.20s, two ArH's ortho to the two acylamino groups; 8.34s, 2H, two ArH's ortho to the two acyl groups.

Preparation of compound 13a

A mixture of compound 11d (6.0 g; 20 mmol), benzylamine (1.1 mL; 10 mmol), Na₂CO₃ (2.1 g; 20 mmol) and acetonitrile (80 mL) was stirred for 24 h at ambient temperature. The mixture remained heterogeneous throughout. The solid material was filtered off, washed successively with water (three portions, 20 mL, each), methanol and ether to obtain 5 g (91%) of compound 13a, m.p. 188-189 °C (BuOH).

C₂₉H₂₇N₃O₈ (545.53). Calcd. C 63.84, H 4.99, N 7.70. Found C 63.20, H 5.04, N 7.83%. IR(KBr): 3170, 1690, 1635 (sh), 695 cm⁻¹.

¹H-NMR: δ 2.22, 6H, two Ac groups; 3.90, PhCH₂; 4.00s, 4H, two Ar-CO-CH₂ groups; 7.2-7.4 m, 7H, Ph + two ArH's *ortho* to the two acetylamino groups; 8.25s, 2H, two ArH's *ortho* to the two acyl groups.

Debenzylation

Compound 13a (2.7 g; 5 mmol) was hydrogenolyzed in dioxane solution (150 mL) in the presence of an 8% Pd-C catalyst. After the uptake of the calculated amount of hydrogen, the mixture was heated to its boiling point and the catalyst was removed by filtration from the hot solution and washed with hot dioxane. The combined filtrate and washings were evaporated to dryness in vacuum. The residue was triturated with a mixture of methanol and ether to obtain 0.9 g (40%) of compound 13b, m.p. 194-195 °C (non-recrystallized). IR (KBr): 1685 and 1620 cm⁻¹, sh.

Ethoxycarbonylation

A mixture of crude 13b (1.0 g; 2 mmol), anhydrous dioxane (100 mL) and ethyl chloroformate (0.8 mL; 8 mmol) was refluxed with continuous stirring until the white suspension turned into a clear yellow solution (about 30 min), which was then poured onto ice (60 g). The aqueous solution was extracted with dichloromethane. The oily residue, obtained after conventional work-up of the dichloromethane solution, was boiled with ethanol (20 mL) and the resulting yellow powder was filtered off from the hot solution to obtain 1.0 g (90%) of compound 13e, m.p. 255-257 °C (non-recrystallized).

 $\rm \tilde{C}_{25}\rm H_{25}\rm N_{3}\rm O_{10}$ (527.47). Calcd. C 56.92, H 4.78, N 7.97. Found C 56.90, H 4.85, N 7.85%. IR (KBr): 1690 and 1630 cm⁻¹.

BERTHA et al.: SYNTHESIS OF QUINAZOLINE DERIVATIVES

Synthesis of the quinazoline derivatives 3d,5b-5d, 6b, 7 and 8

General procedure

The 2'-acylanilides 9d, 10b-10d, 11b, 12c and 13c (0.4-0.8 g) were heated in sealed tubes for 4-5 h at 150 °C with ethanol (10-30 mL) previously saturated at 0 °C with ammonia. In most cases extensive charring took place. The ring closures of several acylanilides were therefore carried out by heating for longer periods at somewhat lower temperatures (see Table I). The reactions normally resulted in mixtures of several compounds (formed in comparable amount) which were worked up by preparative TLC (Kieselgel PF₂₅₄₊₃₆₆; benzene-acetone, 10:1-1:1) or column chromatography (Kieselgel 60, particle size 0.063-0.200 mm; benzeneacetone, 10:1-1:1). Not all by-products were identified. — The reaction mxtures obtained with compounds 10c and 11b contained a single main product (5c and 6b, respectively). These were worked up after treatment with Norite by partly evaporating the solvent and crystallization of the main product, or by evaporation to dryness and recrystallization. For the yields, m.p.'s and analytical data see Table I.

Table I

Starting compound	Yield,	Mp., °C	Molecular formula	Calcd./Found			
Product	%	(recryst. from)	(Mol. wt)	С %	Н %	N %	
9d/3d	38	257 ^b (non-recryst.)	$\substack{\text{C}_{19}\text{H}_{17}\text{N}_{3}\text{O}_{3}\\(335.35)}$			$12.53 \\ 12.66$	
10b/5b	3.2°	185 (acetone)	$C_{21}H_{19}N_{3}O_{5}$	64.11	4.87	10.68	
	35^{d}	(account)	(393.30)	04.30	4.05	10.01	
10c/5c	70	144—145 (acetone)	$\substack{ C_{22}H_{21}N_3O_5\\(407.41) }$	64.85 64.63	$\begin{array}{c} 5.20\\ 5.14\end{array}$	$\begin{array}{c} 10.31\\ 10.60\end{array}$	
10d/5d	31	108—110 (acetone)	$\substack{\mathrm{C}_{28}\mathrm{H}_{25}\mathrm{N}_{3}\mathrm{O}_{6}\\(499.50)}$	67.32 67.60	$5.05 \\ 5.17$	$8.41 \\ 8.47$	
11b/6b	78	156—157 (EtOH)	$\substack{\mathrm{C_{17}H_{15}N_{3}O_{2}}\\(293.31)}$	$\begin{array}{c} 69.61 \\ 69.47 \end{array}$	$\begin{array}{c} 5.15\\ 5.28\end{array}$	$\begin{array}{c} 14.33\\ 14.60\end{array}$	
12e/7	$32^{\rm e}$	151–152 (non-recryst.)	$\substack{\mathrm{C}_{25}\mathrm{H}_{23}\mathrm{N}_5\mathrm{O}_6\\(489.47)}$	$\begin{array}{c} 61.34\\ 61.17\end{array}$	$\begin{array}{c} 4.74\\ 5.01\end{array}$	$\begin{array}{c} 14.31\\ 14.25\end{array}$	
13c/8	$34^{ m e}$	210 (benzene)	$\substack{\text{C}_{25}\text{H}_{23}\text{N}_5\text{O}_6\\(489.47)}$	$\begin{array}{c} 61.34\\ 61.25\end{array}$	$\begin{array}{c} 4.74\\ 4.80\end{array}$	$\begin{array}{c}14.31\\14.28\end{array}$	

Synthesis of the quinazoline derivatives 3d, 5b-d, 6b, 7 and 8^a

 $^{\rm a}$ Reaction time: $4\!-\!5$ h, temperature 150 °C. For the other reaction parameters, see text above.

^b Slight dec. from 240 °C

^o Other identified products: ethyl 4-aminobenzoate (57%), unchanged 10b, 10a, 5a

^d Reaction time 10 h, temperature 100-110 °C

^e Reaction time 12 h, temperature 120 °C

Spectral data

3d: IR (KBr): 3300, 3250 and 1680 cm⁻¹. UV (EtOH): 225 (4.52), sh; 235 (4.57); 320 (3.98), sh; 333 (3.97). ¹H-NMR (DMSO- d_6 : reference: DMSO- d_5 = 2.50): δ 2.0s, Ac; 2.65s, 2-Me; 4.35s, 4-CH₂; 6.2s, OCH₂O; 7.1-7.8 m, ArH's; 9.8 bs, NH. MS (165 °C), m/z (rel. int.): 335 (M^+ , 64), 334 (100), 320 (4.3), 293 (10), 292 (29), 277 (6), 276 (9), 235 (2.8), 234 (5.4), 187 (7), 162 (6), 146 (3.5), 120 (9), 106 (27).

5b: IR (KBr): 1730 and 1680 cm⁻¹. UV (EtOH): 234 (4.53); 2.61 (4.27), sh; 319 (3.94), sh; 334 (3.99). MS (150 °C), m/z (rel. int.): 393 (M^{++} , 7), 365 (60), 364 (45), 350 (4.0), 349 (5.5), 348 (5.7), 336 (10), 320 (10), 216 (10), 202 (100), 189 (28), 188 (61), 178 (25), 160 (8).

348 (5.7), 336 (10), 320 (10), 216 (10), 202 (100), 189 (28), 188 (61), 178 (25), 160 (8), **5c**: IR (KBr): 1730 and 1660 cm⁻¹. UV (EtOH): 224 (4.48), sh; 235 (4.51); 322 (3.82), sh; 333 (3.89). ¹H-NMR: δ 1.4t + 4.35q, COOEt; 2.0 s, N-Ac; 2.6s, 2-Me; 5.35s, 4-CH₂-N; 6.1s, OCH₂O, 7.2s + 7.3s, 5-H + 8-H; 7.3 + 8.0, AA'BB' spectrum, $J_{\text{gen}} = 8.2$ Hz, ArH's of *p*-disubstituted benzene ring. MS (140 °C), *m/z* (rel. int.): 407 (*M*⁺, 70), 365 (27), 364 (100), 336 (5.3), 202 (2.5), 201 (2.9), 189 (5.7), 188 (9), 187 (6.1), 178 (4.5).

5d: IR (KBr): 1730 cm⁻¹, b. UV (EtOH): 227 (4.60), sh; 232 (4.62); 262 (4.27), sh; 319 (4.01), sh; 331 (4.08). ¹H-NMR: δ 1.35t + 4.3q, COOEt; 2.65s, 2-Me; 5.15s and 5.3s, benzyl methylene and 4-CH₂-N; 6.1s, OCH₂O; 7.2s, 7H, Ph + 5-H + 8-H; 7.4 + 7.95, AA'BB', $J_{\text{gem}} \approx 8$ Hz, ArH's of *p*-disubstituted benzene ring. MS (170 °C), m/z (rel. int.): 499 (M^+ , 19), 454 (4.1), 408 (15), 364 (37), 336 (4.5), 291 (2.5), 202 (38), 187 (11), 91 (100).

6b: IR (KBr): 3350; first band in the double bond region 1600 cm⁻¹.

7: IR (KBr): 1685 cm⁻¹. UV (EtOH): 226 (4.55), sh; 233 (4.59); 318 (3.88), sh; 328 (3.96).

8: IR (KBr): 1685 cm⁻¹. UV (EtOH): 226 (4.57); sh; 232 (4.60); 322 (3.82), sh; 331 (3.89). ¹H-NMR: δ 1.29t + 4.18q, J = 7 Hz, COOEt; 2.59s, 6H, two methyl groups; 4.98s, 4H, two 4-CH₂-N groups; 6.04s, 4H, two OCH₂O groups; 7.09s, 2H, and 7.20s, 2H, ArH's.

Attempted cyclization of compound 10a

When the above methods of cyclization (at 150 °C) and work-up were applied to compound 10a, 85% of ethyl 4-aminobenzoate were obtained rather than the desired compound 5a; considerable amounts of tars were also formed.

Reaction of compound 14 with ethanolic ammonia

A mixture of compound 14 (0.8 g; 2 mmol) and saturated ethanolic ammonia solution (20 mL) was heated in a sealed tube for 5 h at 150-155 °C. The solution was allowed to cool and the solvent was partly evaporated to obtain 0.65 g (78%) of crystalline 5c, identical (IR, TLC, m.p.) with an authentic sample obtained as described above.

4-(2-Methyl-6,7-methylenedioxy-4-quinazolinylmethyl)aniline (3c)

A mixture of compound **3d** (0.15 g), ethanol (6 mL) and *conc.* aqueous HCI (4 mL) was refluxed for 2 h. The solution was allowed to cool and made alkaline by the addition of 10% aqueous NaOH (20 mL). The resulting emulsion was extracted with dichloromethane, and the organic phase was dried (MgSO₄) and evaporated to dryness. The residue was taken up in ether and the product (0.10 g; 76%; m.p. 221 °C) was filtered off. For the IR, UV, ¹H-NMR and mass spectra, see Ref. [1].

Ethyl N-[4-(2-methyl-6,7-methylenedioxy-4-quinazolinylmethyl)phenyl]carbamate (3b)

A mixture of compound 3c (50 mg) and ethyl chloroformate (3 mL) was refluxed for 1 h and poured into water (5 mL). The mixture was made alkaline and extracted with dichloromethane. The organic phase was dried (MgSO₄) and evaporated to dryness. The crystalline residue was recrystallized from EtOH to obtain 30 mg of the title compound, 3b, m.p. 169 °C. For the IR, UV, ¹H-NMR and mass spectra, see Ref. [1].

Deacylations and attempted deacetylations of compounds 5b-5d and of ethyl N-(2-methyl-6,7-methylenedioxy-4-quinazolinylmethyl)carbamate (2b)

In the presence of acids

(a) A mixture of compound **5b** (393 mg; 1 mmol), dry ethanol (25 mL) and saturated methanolic HCl (2.5 mL) was allowed to stand for 10 h at ambient temperature; the starting compound was completely used up at this point (TLC). The mixture was made slightly alkaline (10% aqueous NaOH) and evaporated to dryness in vacuum. The residue was taken up in CH_2Cl_2 , and the resulting solution was dried (MgSO₄) and worked up by preparative TLC (Kieselgel PF₂₅₄₊₃₆₆; benzene-acetone, 10:1) to obtain 0.11 g (66%) of ethyl 4-aminobenzoate, m.p. 88 °C, identical (IR) with an authentic sample, and 0.05 g of a non-identified product.

(b) A mixture of compound 5c (213 mg; 0.5 mmol), ethanol (2 mL) and conc. HCl (2 mL) was refluxed for 20 min. The ethanol was evaporated from the resulting red solution in vacuum. The residue was made alkaline (10% aqueous NaOH) and extracted with CH_2Cl_2 . The insoluble material was discarded. The CH_2Cl_2 solution was dried and worked up by preparative TLC (Kieselgel PF₂₅₄₊₃₆₆; benzene-acetone, 1 : 1) to obtain 31 mg (38%) of ethyl 4-aminobenzoate and 32 mg (32%) of 2,4-dimethyl-6,7-methylenedioxyquinazoline [5], both identical (IR) with authentic samples.

(c) A mixture of compound **5c** (517 mg; 1.24 mmol), dry ethanol (25 mL) and saturated methanolic HCl (2 mL) was refluxed for 6 h and worked up by TLC to obtain 129 mg (25%) of unchanged **5c**, 46 mg (22.5%) of ethyl 4-aminobenzoate, traces of 2,4-dimethy-6,7-methylenedioxyquinazoline [5], 13 mg (5.3%) of 2-methyl-6,7-methylenedioxy-4(3H)-quinazolinone [5] and 101 mg (22.4%) of compound **5a** (see below), all of them being identical (m.p.'s, IR spectra, R_f values) with authentic samples. (d)* A mixture of compound **2b** [6] (55 mg; 0.19 mmol), ethanol (3 mL) and conc.

 $(d)^{*'}$ A mixture of compound **2b** [6] (55 mg; 0.19 mmol), ethanol (3 mL) and conc. HCl (2 mL) was refluxed for 30 h, until the starting compound was completely used up (TLC). The solution was made alkaline (10% aqueous NaOH) and extracted with CH₂Cl₂. The organic phase was washed with water until neutral, dried (MgSO₄) and evaporated to dryness. The residue was triturated with a few drops of methanol to obtain 12 mg (31%) of 2,4-dimethyl-6,7-methylenedioxyquinazoline [5]. According to TLC, ethyl carbamate was also present in the reaction mixture.

In the presence of bases

(e) Metallic sodium (10 mg; 0.43 mmol) was dissolved in dry ethanol (5 mL); compound **5c** (0.1 g; 0.23 mmol) was added, and the mixture was refluxed for 1 h, until compound **5e** was completely used up. The solution was evaporated to dryness. The residue was taken up in CH_2Cl_2 and worked up by TLC to obtain ethyl 4-aminobenzoate as the main product in addition to an unidentified minor compound.

(f) Metallic sodium (20 mg; 0.87 mmol) was dissolved in dry ethanol (15 mL); compound **5c** (295 mg; 0.7 mmol) was added, and the mixture was refluxed for 1 h to obtain 35 mg (13.5%) of compound **5a**, m.p. 242-243 °C, which separated in crystalline form on standing overnight in a refrigerator. The filtrate of this product was evaporated to dryness and the residue was triturated with CH_2Cl_2 . The resulting solid (193 mg) was filtered off, taken up in methanol and worked up by TLC (Kieselgel $PF_{254+366}$; benzene-methanol, 3 : 1) to obtain an oily product (145 mg) which, when triturated with dichloromethane, furnished a solid (86 mg; m.p. 212 - 213 °C, dec.). This was dissolved in methanol (about 2 mL). When the methanolic solution was acidified with acetic acid (pH 3-4) and poured into water, 40 mg (15%) of compound **5e**, m.p. 239 °C was obtained.

Compound **5a**: IR (KBr): 3250, 1680, 1595 cm⁻¹. MS (180 °C), m/z (rel. int.): 365 $(M^+, 100)$, 364 (42), 351 (4), 350 (5), 349 (4), 337 (4), 336 (9), 321 (5), 320 (15), 292 (5), 216 (13), 215 (5), 202 (9), 201 (5), 189 (38), 188 (86), 187 (13), 178 (36), 177 (3), 160 (7).

(g) A mixture of compound 5d (0.1 g; 20 mmol), 5% aqueous Na₂CO₃ (2 mL) and ethanol (4 mL) was refluxed for 8 h and the resulting clear yellow solution concentrated to about 1/3

* Experiment carried out by Mrs. G. BARTA-SZALAI.

** Obtained on a Varian XL-100 FT NMR spectrometer.

of the original volume. Water (5 mL) was then added and the mixture was acidified with a few drops of acetic acid to obtain 0.07 g (75%) of compound **5f**, m.p. 217–219 °C. $C_{26}H_{21}N_3O_6$ (471.45). Calcd. C 66.23, H 4.49, N 8.91. Found C 66.12, H 4.57, N 9.20%.

IR (KBr): 3700-2900 with local maxima at 3450 and 2950, 1730 cm⁻¹, b.

¹H-NMR: δ 2.65s, 2-Me; 5.10s + 5.25s, benzyl methylene and 4-CH₂-N; 6.00s, OCH₂O; 7.15s, 7H, Ph + 5-H + 8-H; 7.30 + 7.90, AA'BB' spectrum, $J_{\text{gem}} = 8$ Hz, p-disubstituted benzene ring.

Attempted acid hydrolysis of this product (0.1 g $5f + 1 \,\mathrm{mL\,conc.\,HCl} + 2 \,\mathrm{mL\,AcOH} +$ 3 mL H_oO: 3 h refluxing) furnished only unchanged starting material.

Re-esterification:

Compound 5f (0.05 g) was refluxed for 2 h with a mixture of dry ethanol (5 mL) and conc. $H_2SO_4^{\tau}$ (0.03 mL). After neutralization with 5% aqueous Na_2CO_3 , the mixture was evaporated to dryness. The residue was taken up in CH_2Cl_2 and, after filtration, worked up by TLC to obtain 18 mg (34%) of compound 5d.

(h) Hydrogenolysis of compound 5d

Compound 5d was hydrogenated at room temperature and ordinary pressure in ethanol in the presence of an 8% Pd-C catalyst to obtain a mixture of products which was worked up by TLC. None of the products proved identical (IR) with compound 5a.

Ethyl N-(4-methyl-6,7-methylenedioxy-2-quinazolinylmethyl)-N-phenylcarbamate (6a)

A mixture of compound 6b (0.5 g; 1.7 mmol) and ethyl chloroformate (10 mL) was refluxed for 2 h and evaporated to dryness in vacuum. The residue was recrystallized from EtOH to obtain 0.35 g (56%) of compound 6a, m.p. 187-188 °C.

C20H19N3O4 (365.37). C 65.74, H 5.24, N. 11.50. Found C 65.94, H5.10, N 11.76%.

UV (EtOH): 234 (4.63); 316 (3.77), sh; 330 (3.96).

IR (KBr): 1715 cm⁻¹.

¹H-NMR: δ 1.15t + 4.1q, COOEt; 2.75s, 4-Me; 5.0s, 2-CH₂-N; 6.0s, OCH₂O; 7.15s + 7.20s, 5-H + 8-H; 7.1-7.5m, Ph.

MS (135 °C), m/z (rel. int.): 365 (M⁺, 62), 320 (3.6), 293 (22), 202 (100), 277 (2.5), 276 (3.5), 202 (6.4), 201 (8), 189 (6.3), 188 (5.8), 187 (4.5), 160 (6.3).

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SYNTHESIS AND SPECTRAL CHARACTERISATION OF OXOVANADIUM(IV) COMPLEXES WITH ETHYLENEDIAMINE DERIVATIVES OF 2,2'-DIHYDROXYCHALKONES

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A few complexes of oxovanadium(IV) with ethylenediamine derivatives of 2,2'-dihydroxy chalkones have been prepared in ethanolic medium. They have 1:1 stoichiometry of the type VOL. The molecular weight determination in nitrobenzene reveals that the complexes are dimeric in nature. Appearance of a strong band in the region of 985-970 cm⁻¹ of i.r. precludes the possibility of dimerization through oxygen of VO moiety. The observed magnetic moments (1.73-1.83 B.M.), suggest that the complexes are devoid of spin-spin interactions. The electronic spectra of the complexes in chloroform, DMF and pyridine have been interpreted in terms of WASSON's model suggested for distorted square pyramidal geometry. It appears from the results that donor solvents have no profound effect on the optical spectra of the complexes. Various ligand field parameters viz. Dq, Ds and Dt, and also NSH parameters DQ and DT have been calculated. The degree of distortion, DT/DQ lies in the range of 0.255-0.289.

Introduction

The coordination chemistry of oxovanadium(IV) has been dominated by the ligands containing -N - -O - and -S - donor atoms [1-6]. The magnetic and spectral properties have been instrumental to characterize a large number of complexes. Several generalizations regarding the stereochemistry of oxovanadium(IV) complexes have been proposed on the basis of such studies [6-8]. The theoretical models extended to explicate the spectral and magnetic properties of idealized systems often fall inadequate [9-14]. A few recent communications have evaluated the limitations of such generalizations made thus far.

In this paper we wish to address ourselves to a problem of synthesizing oxovanadium(IV) complexes with branched tetradentates containing -N- and -O- donor atoms.

It is documented in the literature that the branched tetradentate ligands often form polymeric complexes [15]. At this stage our aim is to know whether oxovanadium(IV) forms polymeric complexes with these ligands.

The following ligands were used for preparing oxovanadium(IV) complexes.

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Experimental

Materials and methods

The ckemicals used for preparing the ligands (1-5) were of reagent grade. The substituted salicylaldehydes and o-hydroxy acetophenones were prepared by the known methods [16, 17].

Chalkones were prepared by condensing salicylaldehydes with acetophenones in alkaline medium [18]. These were recrystallized from a mixture of benzene and petroleum ether.

Preparation of ligands

2,2'-Dihydroxychalkones and ethylenediamine in 1:1 molar proportions were mixed in alcoholic medium and refluxed for 2 hrs on a water bath. Crystalline compounds separated on cooling. The reaction mixtures were filtered and recrystallized from alcohol and shining plates were obtained.

Preparation of complexes

To a 0.01 M ligand solution in alcohol 0.01 M vanadyl sulphate monohydrate, and 2.5 g of sodium acetate (anhydrous) were added. The resulting mixture was refluxed for about 3 hrs. The reaction mixture was transferred into a beaker and the complex was precipitated by diluting the former with water. The complex was filtered, washed with water containing small quantity of alcohol and dried in vacuum over fused CaCl₂.

Analysis

Vanadium in the complexes was determined by titration with a standard $KMnO_4$ [19]. Nitrogen in the complexes was accounted for by KJELDAHL method. The results of the elemental analysis are given in Table I.

Physical measurements

The magnetic susceptibilities of the complexes at room temperature were measured, on a GOUY balance using $Hg[Co(SCN)_4]$ as a calibrant. The electronic spectra of the complexes in chloroform, DMF and pyridine were measured on an ELICO spectrophotometer model C1-24 in the 340-900 nm region.

The infrared spectra of the complexes and ligands in Nujol mull were recorded on a Perkin-Elmer 297 spectrophotometer.

Molecular weights of the complexes were determined cryscopically using nitrobenzene.

HIREMATH, KULKARNI: OXOVANADIUM(IV) COMPLEXES

Lig. Comp. No. No.	Comp.	Empirical formula	Analyti	cal data	Molecular wt.		Magnetic moments	
		V (%)	N (%)	Caled.	Found	(B.M.)		
1	6	$(C_{18}H_{18}N_2O_2)VO$	14.00 (14.10)	7.58 (7.75)	360.94	662	1.76	
2	7	$(\mathrm{C_{17}H_{15}ClN_2O_2})\mathrm{VO}$	12.95 (13.35)	7.28 (7.34)	381.44	750	1.73	
3	8	$(C_{19}H_{20}N_2O_2)VO$	13.49 (13.58)	7.56 (7.47)	374.94	702	1.83	
4	9	$(\mathrm{C_{18}H_{17}ClN_2O_2})\mathrm{VO}$	12.67 (12.88)	6.95 (7.08)	395.44	750	1.74	
5	10	$(C_{18}H_{17}CIN_2O_2)VO$	12.96 (12.88)	6.88 (7.08)	395.44	780	1.83	

Table I Elemental analysis, molecular weight and magnetic moments of oxovanadium(IV) complexes

Note: the values given in the parentheses are the calculated ones; the molecular weights are determined in nitrobenzene.

Results and Discussion

The complexes are bluish-green microcrystalline substances and soluble to a limited extent in common organic solvents. These complexes have (Table I) 1:1 stoichiometry of the type VO.L (Where L is a doubly deprotonated ligand.) Molecular weight determinations of these complexes in nitrobenzene focus upon the dimeric nature of the complexes viz. (VOL)₂.

Table II The important infrared frequencies in (cm⁻¹) of oxovanadium(IV) groups and their assignments

Comp. No.	Ethylenic v(C=C)	ν(C=N)	Aromatic $\nu(C=C)$	Phenolic v(C—O)	v(V=0)
6	1630 m	1615 s	1590 m 1535 s	1300 s	985 s
7	1625 m	1610 s	1590 m 1520 s	1300 s	980 s
8	1630 m	1612 s	1590 s 1535 s	1305 m	978 s
9	1630 m	1605 s	1520 s	1310 m	970 s
10	1625 m	1615 s	1590 s 1535 m	1300 s	980 s

s = strong; m = medium.

In the ligands one observes these stretching vibrations in the following regions $\nu(\text{NH}) = 3450 - 3425 \text{ cm}^{-1}$; Ethylenic $\nu(\text{C}=\text{C})$ around 1625 cm⁻¹; Hydrogen bonded OH = 2730 - 2580 cm⁻¹, $\nu(\text{C}=\text{N})$ 1620 - 1613 cm⁻¹ and phenolic $\nu(\text{C}=\text{O})$ = 1289 - 1280 cm⁻¹.

Infrared Spectra

The infrared spectra of the complexes are listed in Table II along with their assignments.

2,2'-Dihydroxy chalkones are marked by the inter- and intra-molecular hydrogen bondings [20]. The inter-molecular hydrogen bonding (3200 cm⁻¹) vanishes when these chalkones are condensed with ethylenediamine. A broad band of medium intensity appears in these ligands in the region 3450-3425cm⁻¹ and has been ascribed to the ν (NH) vibration, on analogy with the assignments in aliphatic primary amines [21]. The weak broad bands with fine structure observed in the region 2730-2580 cm⁻¹ are attributed to the intramolecular hydrogen bondings of the following type. Similar type of hydrogen bondings are encountered in salicylidene-o-hydroxyaniline [17].



The double bonds conjugated to the aromatic system have been thoroughly investigated [22]. In chalkones the v(C=C) vibration has been located around 1625 cm⁻¹ by the earlier workers [20, 23]. In these ligands, we observe v(C=C) as a strong band in the region 1640–1630 cm⁻¹. Another high intensity band observed in the region 1620–1613 cm⁻¹ has been regarded as due to the v(C=N) vibration in view of the previous assignments [24]. A group of medium to high intensity bands in the region 1583–1484 cm⁻¹ is due to the aromatic v(C=C) vibrations. The high intensity band in the region 1289– 1280 cm⁻¹ is assigned to the phenolic v(C-O) vibrations. The absence of this band in benzylideneacetophenone-ethylenediamine confirms the assignments.

We observe the following changes in the characteristic frequencies which mark the complex formation.

1. The v(NH) appears as a weak band at 3400 cm⁻¹. This weakening may be attributed to the coordination of NH₂ group to the metal ion.

2. The bands due to the intramolecular hydrogen bonded OH do not appear in the complexes.

3. The phenolic $\nu(C-O)$ vibration is observed in the 1310-1300 cm⁻¹ region. These observations imply that the ligands complexed with oxovana-dium(IV) via deprotonation.

4. The band due to the v(C=N) appears in the 1615-1605 cm⁻¹ region suggesting that coordination to the oxovanadium(IV) has taken place through nitrogen of the azomethine group.

The sharp broad band appearing in the region $985-970 \text{ cm}^{-1}$ for these complexes is attributed to the $\nu(V=0)$ vibration [25]. That the dimerization

can occur also through the oxygen of V=O moiety has been ruled out for these complexes in view of the located position of the v(V=O) band [1, 9].

Magnetic Data

The magnetic moments obtained for these complexes at room temperature are given in Table I.

The $\mu_{\rm eff}$ values obtained for these complexes fall in the range of 1.73— 1.83 B.M. These are very close to the spin-only value of 1.73 B.M. for oxovanadium(IV) when the orbital contribution is quenched [26]. The results preclude the existence of exchange interactions in the complexes.

Electronic Spectra

The observed band maxima for these complexes in chloroform, DMF and pyridine are systematized in Table III along with the ligand field and NSH parameters.

The electronic spectra of the complexes in various solvents exhibit absorption bands in the regions: $12\ 500-13\ 890$, $16\ 390-17\ 860\ \mathrm{cm}^{-1}$ and $26\ 320-27\ 030\ \mathrm{cm}^{-1}$. Several models have been proposed to interpret the electronic spectra of oxovanadium(IV) complexes [9-14]. Of them, we have chosen WASSON'S model [14] to interpret the spectral results. According this model the energy level order is the following $d_{xv} < d_{vz} < d_{xz} < d_{x^2-v^2} < d_{z^2}$. Except for the splitting of d_{yz} and d_{xz} levels, the scheme is similar to that of BALLHAUSEN and GRAY [10]. WASSON'S model is a better fit for complexes having distorted square pyramidal geometry, that comes into existence due to the non-equivalence of the donor atoms. The assignments of various bands according to this scheme are shown in Table III. The difference between $v_1(12\ 500-13\ 890\ \mathrm{cm}^{-1})$ and $v_2(16\ 390-17\ 860\ \mathrm{cm}^{-1})$ is approximately 4000 cm^{-1} and is consistent with the prediction of this model. The fourth band due to the $d_{xy} \rightarrow d_{z^2}$ transition appears in the far uv region. This band for these complexes cannot be assigned because of the limited range of the spectrophotometer.

Various ligand field parameters are calculated for these complexes (Table III), and the extent of tetragonal distortion has been calculated using Dq and Dt values, by applying NSH hamiltonian theory of LEVER and coworkers [27, 28]. The ratio of DT/DQ is a measure of tetragonal distortion. The values obtained for these examples are in the range of 0.225-0.283, these values are small compared with the reported value for the limiting case of tetragonally distorted molecule, *i.e.* 0.4226. Thus the complexes are moderately distorted.

Comp. No.	Solvents	$d_{xy} \xrightarrow[\nu_1]{} d_{yz}$	$d_{xy} \xrightarrow{\nu_2} d_{xz}$	$\mathrm{d}_{xy} \xrightarrow[\nu_3]{} \mathrm{d}_{x^2-y^2}$	Dq	Ds	Dt	DQ	DI	D7/DQ
1	Chloroform	12 820	16 390	26 320	1639	-3250	614	35 207	8 320	0.236
	DMF	12 500	16 670	26 320	1667	-3164	602	36 169	8 157	0.225
2	Chloroform	12 500	16 670	26 320	1667	-3164	602	36 169	8 157	0.225
	DMF	13 890	16 670	27 030	1667	-3464	700	34 598	9 485	0.274
	Pyridine	12 820	$17\ 240$	26 320	1724	-3128	687	36 373	9 308	0.256
3	Chloroform	12 500	16 670	26 320	1667	-3164	602	36 169	8 157	0.255
	DMF	13 160	16 950	26 320	1695	-3218	701	35 351	9 498	0.263
4	Chloroform	12 820	17 240	26 320	1724	-3128	687	36 373	9 308	0.256
	DMF	13 150	17 860	27 030	1786	-3190	718	37 580	9 729	0.259
	Pyridine	13 510	16 950	26 320	1695	-3268	741	34 710	10 041	0.289
5	Chloroform	12 820	17 240	26 320	1724	-3128	687	36 373	9 308	0.256
	DMF	13 160	17 860	26 320	1786	-3177	726	37 452	9 837	0.263
	Pyridine	13 150	16 950	26 320	1695	-3268	741	34 710	10 041	0.289

Table III								
The electronic spectra	and ligand field parameters of oronanadium	IV) complexes						

1

It is apparent from the spectral results (Table III), that the donor solvents viz. DMF and pyridine do not exercise much effect on the complexes.

The elemental analysis, molecular weight, magnetic and spectral measurements indicate that these complexes are dimeric and of distorted square pyramidal configuration.



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MICRODETERMINATION OF NIOBIUM(V) WITH IMIPRAMINE HYDROCHLORIDE

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A spectrophotometric method for the determination of microgram amounts of niobium(V) is described. The method is based on the formation of niobium(V) thiocyanate in the reaction between niobium(V) and thiocyanate in acid medium and its extraction into chloroform as an ion pair with imipramine hydrochloride. The molar absorptivity of the complex at 398 nm is 2.24×10^4 L mol⁻¹ cm⁻¹ and spectrophotometric sensitivity is $0.0042 \ \mu g$ Nb(V) cm⁻² for absorbance = 0.001. This method can be applied for the determination of niobium in the range $0.2-3.5 \ \mu g$ mL⁻¹.

Introduction

Numerous methods are available for the determination of niobium(V). The various reagents proposed for the spectrophotometric determination of Nb(V) are thiocyanate [1], chlorosulphophenol S [2], 4-(2-pyridylazo) resorcinol [3], 8-hydroxy-7-(p-tolylazo) quinoline-5-sulphonic acid [4], tribenzylamine [5], azo-dyestuffs [6], catechol and diphenhydramine [7], sulphonitrazo E [8], xylenol orange [9], acid chrome violet K [10], o-dihydroxy coumarins [11] and tetraphenyl arsonium chloride [12]. Atomic absorption spectrophotometric [13-17], chromatographic [18-22], fluorometric [23] and ion-exchange [24] methods have also been used for the evaluation of Nb(V).

Most of the reagents proposed for the spectrophotometric determination of Nb(V) are unsatisfactory for one reason or another. Many reagents require either heating or a long time for maximum colour development. Our investigations revealed that imipramine hydrochloride (IM.HCl) which does not react with Nb(V) in HCl medium forms a chloroform soluble light yellow solid mixed ligand complex instantaneously with the Nb(V)—SCN complex.

The present communication reports the effect of thiocyanate on the extraction of Nb(V) with IM.HCl and proposed IM \cdot HCl for the rapid determination of Nb(V). A procedure has been developed for the microdetermination of Nb(V) from its salt solution and some synthetic mixtures corresponding to

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niobium stabilized steels. The composition of the extractable species has also been determined. The method is simple, rapid, reasonably selective and can be performed at room temperature.

Experimental

Apparatus and reagents

Apparatus. Absorptiometric measurements were made on a Beckman Model DB spectrophotometer and in 10 mm silica cells.

Niobium (V) solution. A stock solution of Nb(V) was prepared by fusing 100 mg of specpure niobium pentoxide with 2.8 g of AnalaR potassium pyrosulphate in a platinum crucible, cooling the melt and dissolving it in 10% tartaric acid solution. The solution was diluted to 250 mL with 10% tartaric acid solution. The stock solution was further diluted as needed. Imipramine hydrochloride solution. A 0.02 M solution of IM.HCl was prepared in chloroform. Thiozyanate solution. A 2.0 M solution of ammonium thiocyanate was prepared in double-distilled water.

All other reagents were of analytical grade and used without further purification.

General procedure

To an aliquot of the stock solution containing $2.0-35.0 \ \mu g$ of Nb(V) 6 mL of 2.0 M ammonium thiocyanate and enough concentrated hydrochloric acid were added to make the acid strength 3.0 M. The total volume of the aqueous phase was made up to 30 mL with double-distilled water. After 2 min this was shaken with 5 mL of IM.HCl solution in chloroform for about 5 min and allowed to stand for the layers to separate. The yellow chloroform layer was separated, diluted to 10 mL with chloroform and dried over anhydrous Na₂SO₄. The absorbance of the chloroform solution was measured at 398 nm against similarly processed reagent as a blank. The amount of the metal extracted was calculated from the appropriate calibration curve.

Results and Discussion

Spectral properties of the complex

The absorption spectrum of the golden-yellow Nb(V)-SCN-IMH complex has an absorption maximum at 398 nm. The Sandell's sensitivity of the complex at 398 nm is 0.0042 μ g/cm² and the corresponding molar absorptivity is 2.24×10^4 L mol⁻¹ cm⁻¹. The system obeys the Beer's Law within a range of 0.2-3.5 μ g Nb(V)/mL of chloroform. The standard deviation of the method is ± 1.24 and the colour of the complex is stable for at least 48 hr.

Extraction of Nb(V) by $IM \cdot HCl$

The IM \cdot HCl forms an intensely yellow-coloured ion-association complex with the binary Nb(V)—SCN complex in hydrochloric acid medium. The ion-association complex can be extracted into chloroform while the binary Nb(V)—SCN complex cannot be extracted under the experimental conditions.
The effect of ligand concentration was examined by measuring the absorbance of solution containing 2 ppm of Nb(V) and various amounts of thiocyanate and IM · HCl. The complete complex formation takes place in 4-12 mL of 2 M NH₄SCN and 2-7 mL of 0.02 M IM \cdot HCl. For quantitative extraction of the ion-association complex, the hydrochloric acid concentration should be between 2.0 and 5.0 M.

Amongst the several solvents tried, viz., benzene, toluene, o-dichlorobenzene, carbon tetrachloride, isoamyl alcohol, isobutanol and chloroform, the last was found to be the most suitable. Under the optimum concentrations of acid, thiocyanate and $IM \cdot HCl$, a time of 5 min was adequate for the quantitative extraction of niobium. A single extraction with chloroform was sufficient to remove all Nb(V).

Ion added	Amount tolerated* (µg)	Ion added	Amount tolerated* (µg)
Chloride	$4.1 imes10^5$	Hg(II)	$2.5 imes 10^3$
Bromide	$2.1 imes10^4$	Au(III)	$2.2\! imes\!10^3$
lodide	$3.0 imes10^3$	Os(VIII)	$3.2\! imes\!10^3$
Fluoride	$2.5 imes10^3$	Ti(IV)	3
Fluoride	$1.3 imes 10^{4a}$	Ti(IV)	$1.2\! imes\!10^{3\mathrm{b}}$
Sulphate	$4.0 imes 10^{4}$	Fe(III)	5
Phosphate	$2.5 imes 10^3$	Fe(III)	$2.0 imes10^{2}$
Acetate	$5.5 imes10^4$	V(V)	2
Citrate	$2.0 imes10^{4}$	V(V)	$2.5 imes10^{2c}$
DMG	$2.3\! imes\!10^4$	W(V1)	60
EDTA	$7.0 imes10^3$	Ta(V)	25
Cr(II)	$1.2\! imes\!10^3$	Ta(V)	$1.0 imes10^3$
Cu(II)	$4.0 imes10^3$	Zn(II)	$3.0 imes10^4$
Co(III)	$2.1\! imes\!10^3$	Rh(III)	$2.2\! imes\!10^3$
Ni(II)	$4.0 imes10^3$	Pd(II)	$6.0 imes10^2$
Mn(II)	$1.9\! imes\!10^3$	Pt(IV)	$1.3 imes 10^3$
$UO_2(II)$	$2.8\! imes\!10^3$	Mo(VI)	40
Pb(II)	$4.0 imes10^3$	Zr(IV)	$4.1 imes 10^3$

Table I

Effect of different ions on the determination of 20 μ g of niobium(V)

* Amount causing an error of less than 2.5%.

^a In the presence of 2 mL 10 M H₂SO₄ ^b In the presence of 2 mL 20 vol% H₂O₂ ^c In the presence of 0.5 g of NaHSO₃ and

^d In the presence of 20 000 μ g of DMG

Effect of various ions

In order to study the effect of various ions in the quantitative determination of Nb(V), an aliquot (5 mL) of solution containing various amounts of foreign ions and 20 μ g of Nb(V) was treated exactly as in the recommended procedure. The results are given in Table I. The presence of Ti(IV), Fe(III), V(V) and Ta(V) can be tolerated up to 3,5,2 and 25 μ g, respectively. The interference of Ti(IV) can be eliminated by adding 2 mL of 20 vol% H₂O₂, Fe(III) by adding 0.5 g of NaHSO₃ and V(V) and Ta(V) by adding 20 000 μ g of DMG; Ti(IV), Fe(III), V(V) and Ta(V) do not them interfere in amounts up to 1200, 200, 250 and 1000 μ g, respectively. Molybdenum(VI) and W(VI) can be tolerated up to 40 and 60 μ g, respectively. Anions such as chloride, sulphate and acetate do not interfere in amounts up to 40 000 μ g; bromide, citrate and DMG up to 20 000 μ g and fluoride, iodide and phosphate up to 2500 μ g.

Composition of the complex

In order to identify the ion-association complex species concerned in the determination of Nb(V), the reaction was investigated. The composition of the complex with respect to Nb(V) and IM \cdot HCl was found to be 1 : 1 [Nb(V) : IMH] by the method of continuous variation [25]. This composition was supported from the plot of log D vs. log [IM \cdot HCl]_{org} at 5.0 M acidity which gave a slope one. A slope of four was obtained from the plot of log D vs. log [NH₄SCN] at constant IM \cdot HCl concentration indicating a 1 : 4 ratio with respect to Nb(V) and thiocyanate. Thus, the probable extractable species in this system is [IMH⁺, NbO(SCH)⁻₄] in which IM \cdot HCl molecule is associated through niobyl oxygen atom. From the results is can be concluded that only the ion-pair formed according to

$$IM \cdot HCl \rightleftharpoons IMH^+ + Cl^-$$
$$IMH^+ + NbO^{3+} + 4 SCN^- \rightarrow [IMH^+, NbO(SCH)_4^-]$$

is extractable into chloroform under the conditions recommended.

Practical Applications

The method has been applied for the determination of niobium in some synthetic samples corresponding to niobium stabilized stainless-steels [26, 27]. The composition of the samples and the percentage of niobium recovered are given in Table II. The interference of Fe(III) can be eliminated by extraction with three 5 mL portions of diethyl ether [28] and the other ions by the methods

Table II

Synthetic	General	Nb, %		
sample	composition, %	Reported	Found*	
1	Mn-0.66, Ni-13.08, Cr-17,20, Mo-0.03, Cu-0.06, V-0.03, W-0.04	0.71	0.70	
2	Cr-17.4, Ni-13.1, Ta-0.006, Mo-0.11, Cu-0.12, Co-0.05	0.91	0.89	
3	Mn-0.15, Cr-18.5, Ni-11.5, Cu-0.05, Ta-0.03, Mo-0.05	0.60	0.58	
4	Cr-18.8, Ni-12.1, Cu-0.1, Mo-2.89	0.80	0.78	

Determination of Nb in synthetic mixtures corresponding to niobium stabilized stainless-steels composition

* Average of five determinations

explained in the effect of different ions. Thus the proposed method is one of the most rapid, sensitive and selective methods for the quantitative determination of microgram amounts of Nb(V).

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COMPUTER-AIDED STRUCTURE ELUCIDATION, II*

¹H-NMR DATA INTERPRETATION

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A computerized ¹H-NMR data interpretation system has been developed using the artificial intelligence approach. An attempt has been made to overcome the difficulties of interpreting higher order spin systems. Proton-containing functional groups are divided into subgroups according to their spectroscopic behaviour and the information they bear. Spin simulation is used to study the effect of substituents on the higher order splitting patterns. Illustrative examples are given.

Introduction

The outstanding role of ¹H-NMR spectroscopy in the structure elucidation of organic molecules has been well known for long; however, there have only been few attempts for computerized interpretation of ¹H-NMR spectra. Reasons for this are: (1) the chemical shift range is small, therefore the characteristic ranges of protons in different chemical (magnetic) environments often overlap, *i.e.* the number of characteristic absorptions is rather low relative to other spectroscopic techniques; (2) splitting pattern caused by scalar spin-spin interactions depend strongly on the $\Delta v/J$ ratio, and at present we have no method for the estimation of its value; (3) chemical shift values are dependent on the solvent, concentration and temperature, and this may also cause different splitting patterns for the same functional group; (4) molecular motions (dynamic behaviour of the molecules) may also cause the averaging of chemical shifts for diastereotopic protons (e.g. AB \rightarrow A₂ and vice versa).

Probably for these reasons previous studies [1-3] on the computerized interpretation of ¹H-NMR spectra restricted the problem to the first order patterns. As a consequence, a great amount of spectral information was lost.

We attempted to overcome this problem using an approach capable of handling both first and higher order spin systems. As our starting point was the ASSIGNER system [4-6, 9], already in operation at our Institute, we

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^{*} For part I, see Ref. [4]

had no intention to prepare a program which can give a reasonable final result (we doubt whether it is possible at all) on the basis of ¹H-NMR data alone. This paper presents a discussion of our results.

Results and Discussion

It is common in ¹H-NMR spectroscopy to classify protons according to their chemical, and consequent spectroscopic behaviour. Protons attached to carbon atoms usually give sharp resonance lines and take part in scalar spin-spin interactions, provided that this is possible at all. Protons bonded to hetero atoms (N, O, S) often produce broad lines, and are ready partners in fast exchange processes.

We followed this classification, and divided proton-containing functional groups into two subgroups (see Fig. 1). Group 1 is divided further, namely to group 1a, in which protons are identical and/or far enough from other



Fig. 1. Classification of proton-containing functional groups according to their spectroscopic behaviour and importance for the joint ${}^{13}C{}^{-1}H{}^{-1}H{}^{-1}R$ interpretation [9]

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pioton(s) to show any spin-spin interaction. Such functional groups were left out of considerations as "less informative" from the point of view of the ASSIGNER system. To Group 1b belong fragments showing spin-spin interaction.

The operating sequence of our program for the interpretation of ¹H-NMR spectra is shown in Fig. 2.

Required inputs are; chemical shifts and relative intensites (obtained as printer outputs), proton allocations (calculated manually from the spectrum integral) and the empirical formula. These data are fed in the computer by means of punched cards.

First the assignment of the hetero protons H(X) is carried out, either, automatically or manually. For the automatic way two spectra recorded at different temperatures are required.



Fig. 2. Flow chart of ¹H-NMR data interpretation

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The program subtracts the two spectra from each other, and the lines shifted more than 0.1 ppm are assigned to H(X) protons. As the general validity of this method is questionable, one may reassign the H(X) protons, manually, considering other spectroscopic evidence, e.g. that from deuteration experiments. In the second step (functional group analysis), groups consistent with the spectroscopic data are selected. For this purpose we use empirical spectral feature-structural fragment correlations. These are store in property matrices, one each for H(X) and H(C) protons. Depending on the nature of the spin-spin interaction, one or more rows of the property matrix stand for a functional group.

The correlations stored originate in part from literature data [7], and in part from our own experience.

At present we have rather few correlations coded (approx. 90), but by the very nature of artificial intelligence systems [8], one can add a new entry very easily. The features included into the property matrix (see Fig. 3) are as follows:

Functional group	Proton allocation in ð1-ð2 range (ppm)	Reference Line range (ppm)	Line num- ber	Relative chemical shifts (ppm)	Relative intensity (°/。)	Number of con- ditions	Number of condi- tions to be ful- filled
-C-O-CH ₂ -CH ₃		1	1	+0.17 ± Δ ₁	29 ± Δ ₂		
	_ ≥ 2	4.35-	2	+0.08 ± Δ1	94 $\pm \Delta_2$		
C-3, H-5, O-2	ð ₁ = 4.50	4.10	3	0	100	4	3
Identifier : 2110	$\delta_{2} = 4.00$		4	-0.09 ± Δ1	33 ± Δ ₂		
Solvent : * * CDCl ₃						_	

* Protons to which the features refer

* * Different property matrices are used for different solvents to eliminate the problems arising from different chemical shifts

Fig. 3. Features included in the ¹H-NMR property matrix

Reference line; usually the strongest line of a spin system is selected for this purpose; the identification of a spin system is based above all on finding a line which fulfils the requirement of the reference line. Chemical shifts and intensities of the other lines of the spin system are given relative to this. *Proton allocation*; this means the number of protons requested in the given range.

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Relative chemical shifts; chemical shift values of the other lines relative to the reference line, in ppm. A $\pm \Delta_1$ range is allowed to compensate for the measuring error and substituent effects.

Relative intensity; the reference line intensity is equal to 1, the intensity of the other lines is given relative to this in percentage. The measured intensity value should be within a $\pm \Delta_2$ range of the value given in the property matrix, otherwise the condition is not fulfilled.

Number of conditions equals the number of expected lines of the spin system in question.

Number of conditions to be fulfilled; number of fulfilled conditions required to put the functional group on the "possible" list.

By means of the above feature we are able to describe also higher order spin systems. In these cases the spin simulation of the system in question has proved a valuable tool for studying the effect of substituents on the splitting pattern. Thus we could estimate the expected changes of line intensities



Fig. 4. The effect of $v_A - v_B$ on the splitting pattern of an ABX₂ (trans) system. (a) $v_B = 504$ Hz, $v_A = 528$ Hz; (b) $v_B = 476$ Hz, $v_A = 528$ Hz. (Curves obtained by spin simulation, using the SIMEQ^{*} program by Varian Associates, Palo Alto.)

and reference line ranges as a function of the substituents not taking part in the spin-spin interaction. To illustrate this point the ABX_2 system was chosen as an example (see Fig. 4).

In the case of the R_1 -CH=CH-CH₂- R_2 fragment (in most cases an ABX₂ system) the property matrix will contain three rows, one each for the

A, B and X protons. All of them are required for the $R_1-CH=CH-CH_2-R_2$ group to survive. Using different J_{AB} values (the coupling constants are converted into relative chemical shift values), we can also distinguish between geometric isomers E and Z.

In order to be selective, the reference line ranges, apart from that of the H(X) protons, are rather narrow, but with the increasing number of spectral lines (higher order spin systems), this requirement becomes less serious. For this reason, in the case of a spin system of ten lines, the reference line ranges are relatively wide to compensate for the unknown character of the R substituents. In other words, the greater the number of expected spectral lines, the smaller the danger of finding a functional group which is not present.

If for some reason, e.g. owing to solvent or magnetic environmental effects, the reference line is shifted outside the expected range, the functional group in question will be lost finally. To avoid this error we use different property matrices for the different solvents (at present we have two, one each for the spectra obtained in CDCl₃ and C_6D_6 solutions, respectively), and we try to define the environment of the proton(s) in question as precisely as possible. Normally the α -groups are exactly described, and often the β -neighbours are also given.

In the case of H(X) protons (Group 1b) there is no other possibility for further filtering therefore the result of functional group analysis is final.

For H(C) protons (Group 2) spin-spin interactions give a further possibility to prune out inconsistent ones. This is done in the step "Check for internal consistency" (cf. Fig. 2) by means of BOOLEAN type logic expressions. The functions included comprise the commonest logical steps of human interpretation of spectroscopic data. We store these expressions in a condition matrix [4].

Functional groups which fulfill the conditions are given as final results of the H(C) proton interpretation. To illustrate the operations of the condition matrix, a simple example is given in Fig. 5.

Examples are given below to illustrate the efficiency of the program described :



Fig. 5. Operation of the ¹H-NMR H(C) condition matrix

Example 1



In this case the following functional groups are permitted using the H(C) matrix:

(1) AROM-ethyl, $-C^*H_3$ (2) 2,6-diethylanilide $-C^*H_3$ (3) $-CO-O-CH_2-CH^*_3$ (4) $R-O-CH^*_2-CH_3$ (5) $R-O-CH_2-CH^*_3$ (6) $-S-CH_2-CH^*_3$ (7) $-N-CH_2-O-CH_2-CH_3^*$ (8) $-NCO-CH_2-CH_3^*$ (9) $-NCO-CH_2-CH_3^*$ (10) $-NCO-CH(CH_3)_2^*$ (11) 2-chloroanilide

After filtering according to the condition matrix, six of the eleven groups are pruned out. The surviving groups are as follows:

The first two pairs of groups suggest the presence of an $R-O-CH_2-CH_3$ and an $-NCO-CH_2-CH_3$ group, respectively, as the pairs are counterparts of each other. In addition, an *ortho*-chloroanilide fragment is allowed (an ABCD spin system).

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* Asterisks i ndicate the protons in question

Example 2



The program suggested the presence of the E from $[R_1-CH=CH--CH_2-R_2(E)]$. No other group was found.

Example 3

 $\stackrel{\mathrm{CH}_{3}}{\longrightarrow} \stackrel{\mathrm{CH}_{3}}{\longrightarrow} \mathrm{CH}_{2} \stackrel{\mathrm{CH}_{3}}{\longrightarrow} \mathrm{CH}_{3}$ Н0-

Result of H(C) matrix : 1,4-disubstituted benzene ring

(the sec.-butyl group is not included yet in the matrix) Result of H(X) matrix : (1) R-OH (associated) (2) AROM-OH

Example 4



Result of	Result of
H(C) matrix:	H(X) matrix :
	(1) $R-OH$
$-\mathrm{CO}-\mathrm{O}-\mathrm{CH}_{2}\mathrm{CH}_{3}$	(2) $R - NH -$
	(3) $R - NH_2$

The above examples verify that our approach of deriving spectral information also from higher order spectra is valuable in many cases. The results obtained are by no means exhaustive considering the capacity of H-NMR spectroscopy, however, the property matrices are extendable practically infinitely.

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Conclusions

The program developed is capable of printing a list of functional group that may be present in an unknown organic molecule on the basis the ¹H-NMR spectrum and the empirical formula. The program has been in use since the summer of 1980 and tested on 120 compounds. On the average, for coupled H(X) protons the output contains 1.1-1.4 times more functional groups than are really present.

For uncoupled H(C) protons this ratio is much less favourable, owing to the lack of filtering based on spin-spin interactions. For our purpose — the identification of greater fragments and the printing of possible H(X) protons - the results are promising. By the extension of the data base, different improved approaches may become possible.

As to the limitations of the present program, the results obtained for molecules containing phosphorus, fluorine or other I = 1/2 nuclei, can be misleading. Also, the program cannot cope with the problem of a mixture of conformers, and the results obtained for molecules taking part in exchange processes with rates in the range of the NMR time scale, may be incorrect.

The list of H-NMR correlations and conditions is available from the authors on request.

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COMPUTER-AIDED STRUCTURE ELUCIDATION, III*

EXTENDED VERSION OF ASSIGNER SYSTEM

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Computer-aided interpretation of ¹³C-NMR, ¹H-NMR and IR spectra of organic molecules (M.W. \leq 500) is done by an artificial intelligence approach. A procedure for the joint ¹³C-NMR⁻¹H-NMR⁻¹R spectrum interpretation is outlined. Possible ways of finding acceptable greater fragments on the basis of ¹H-NMR⁻¹³C-NMR data and of ¹³C-NMR data alone are also described.

Examples have been worked out in detail to demonstrate the capability of the system.

Introduction

In our previous papers [1-3] we presented results concerning an artiticial intelligence spectrum interpretation system. The earlier version of the proposed ASSIGNER program package included the interpretation of ¹³C-NMR and IR spectra. A drawback of this version was that often even the relatively small excess of possible functional groups allowed the generation of an unacceptable high number of structural isomers.

In order to reduce further the number of possibly present groups, we extended the ASSIGNER with a program evaluating ¹H-NMR spectra [4]. The advantage of this step is twofold: on one hand, ¹H-NMR data can be used in the filtering processes [protons bonded to hetero atoms, H(X)]; on the other, scalar spin-spin interactions can be used as structural proofs for the presence of greater structural fragments [protons bonded to carbon atoms, H(C)].

As an aid we developed two subroutines, one for the calculation of the number of benzene rings and its substituents [5] (if any) and, the second, to generate all possible greater fragments on the basis of ¹³C-NMR data (e.g. olefinic double bounds, ethers, pyridine and furan rings). At the same time, in the case of fragments of heterocyclic rings this subroutine will eliminate inconsistent data.

* For parts I and II, see Refs. [1] and [4]

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The output of the present extended version is a list of possible functional groups obtained on the basis of a joint interpretation of ¹³C- ¹H-NMR and IR data; in addition, a list of the possible greater fragments are also given.

Here we give a short description of the operation and results obtained with the extended version.

Results and Discussion

Joint ${}^{13}C - {}^{1}H$ -NMR - IR interpretation

The flow chart of the extended version is given in Fig. 1.

Details and principles of ¹³C-NMR — IR data interpretation we have already reported elsewhere [1, 2]. The proton-containing functional groups are classified according to the nature of the proton(s) they contain. Only those having proton(s) attached to hetero atoms (O, N, S) are considered in the joint ¹³C — ¹H-NMR — IR interpretation (see Fig. 1). The result of functional group analysis, *i.e.* the fragments consistent with the elementary analysis and spectroscopic data, are confronted directly with the joint ¹³C-NMR — IR list by means of a ¹³C — ¹H — IR condition matrix similar to that described in the preceding paper [4].

Example 1

$$\begin{array}{ll} \mathrm{X} = \mathrm{R-COOH} & \mathrm{A} = (\mathrm{AL}) - \mathrm{COOH} \\ & \mathrm{B} = (-\mathrm{CH}_2) - \mathrm{COOH} \\ & \mathrm{C} = (\mathrm{R}) - \mathrm{COOH} \\ & \mathrm{D} = (\mathrm{R}) - \mathrm{COOH} \\ & \mathrm{E} = -\mathrm{COOH} \end{array} \right\} \ \mathrm{IR} \\ & \mathrm{IR} \\ \end{array}$$

ogical equation: $X = A + B + C \ arrow D \ brack E$

where: AL = aliphatic carbon atom, R = any carbon atom, + = logical "or", * = logical "and", () = possible adjacent group

Example 2

$$\begin{array}{ll} \mathbf{X} = -\mathbf{C} {=} \mathbf{N} {-} \mathbf{O} \mathbf{H} & \mathbf{A} = (\mathbf{N} {=}, \mathbf{C} {=}) {=} \mathbf{N} {-} \mathbf{O} \mathbf{H} & \mathbf{I} \mathbf{R} \\ & \mathbf{B} = {-} \mathbf{C} {=} \mathbf{N} {-} \mathbf{O} \mathbf{H} & {}^{13} \mathbf{C} {-} \mathbf{N} \mathbf{M} \mathbf{R} \\ & \mathbf{C} = {=} \mathbf{N} {-} \mathbf{O} \mathbf{H} & {}^{14} \mathbf{H} {-} \mathbf{N} \mathbf{M} \mathbf{R} \end{array}$$

ogical equation: X = A * B * C



ASSIGNER final result

Fig. 1. Flow chart of the extended ASSIGNER system

For example, to confirm or to diminish the probability of an R-COOH group, the program looks for the presence of one of the three groups A, B or C in the IR, for D (¹³C-NMR) in the joint ¹³C-NMR - IR list, and for E in the ¹H-NMR H(X) list. This procedure will eliminate functional groups inconsistent with any of three spectroscopic methods.

Interpretation of the ¹H-NMR H(C) result

Functional groups containing protons bonded to carbon atoms do not take part in the joint interpretation, unlike H(X) protons.

Fragments which survived the internal consistency check (see Fig. 1) are checked again using ¹³C-NMR data of the joint ¹³C-NMR — IR list. Here again a condition matrix (¹H — ¹³C condition matrix) is employed to complete the task of filtering. An example is given below.

X = 2,6-diethylanilide [¹H-NMR, H(C)] X = A * B * C * D * E * F * G (logical equation)

	Requested ¹³ C-NMR functional groups	Number of identical carbon atoms	Number of groups required
A	- CO $-$ N $-$	1	1
в	1C-AROM-C-1	1	2
С	1H-AROM-C-1	1	1
D	1H-AROM-C-1	2	1
E	1N-AROM-C-1	1	1
\mathbf{F}	$-C - C^*H_2 - C -$	2	1
G	$-\operatorname{CH}_2\!-\!\operatorname{C*H}_3$	2	1
		1	

(1C-AROM-C-1 means a carbon atom of a benzene ring to which an another carbon atom is bonded; ¹H-AROM-C-1 denotes an unsubstituted benzene ring atom; 1N-AROM-C-1 means a carbon atom of a benzene ring to which a nitrogen atom is bonded, *etc.* Asterisks indicate the carbon to which the conditions refer.)

The logical equation has the same role as before, but two additional features (number of identical carbon atoms and number of required groups) have been included, taking into account thereby quantitative information also. For instance, in the above case at least two B groups (but in different chemical environments), and two each from the D, F and G group (in identical chemical environment), *etc.*, should be present: otherwise the X group will be pruned out.

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As described earlier [4] the correlations included in the H(C) property matrix are restricted to those groups in which spin-spin interactions exist.

We utilize these interactions in finding greater structural fragments. Remember [1, 3] that ¹³C-NMR correlations were used to identify a carbon atom in a specified chemical environment, but there was no information obtained on the nature (tertiary, secondary, *etc.*) of the neighbouring carbon atoms. The immediate conclusion is that probably present greater fragments (see Fig. 1) obtained this manner represent a different quality of information as compared with the joint ¹³C – ¹H-NMR – IR result. When there is no reason to cancel any of the obtained possible greater fragments, they are informational homologues.

Finding probably present greater fragments on the basis of ¹³C-NMR data

We tried to construct criteria for the presence of greater fragments also using ¹³C-NMR data alone. For this purpose we used another condition matrix, called *carbon greater fragment* condition matrix.

The basic idea of its operation is rather simple. Each row of the matrix corresponds to an assumed greater fragment, and provided that the program finds in the list of the ¹³C-NMR — IR data all the required building blocks (functional groups) listed in the given row, the fragment will be declared as "possible". It is obvious that all the building blocks of the fragment in question should be in the basic ¹³C-NMR property matrix, otherwise the matrix is not effective. For illustration an example is given below.

Assumed fragment:

 $\mathbf{R}^{1} \xrightarrow{\begin{array}{|c|c|} 4 & 3\\ 5 & 2 \end{array}} \mathbf{R}^{2}$

Unsymmetrically 2,5-disubstituted furan ring

Required functional groups: Juran C2 subst. -O-C =Juran C2 subst. -O-C =

uran	62	subst.	-0-c=
J _{uran}	C 3		-CH =
Juran	C3		-CH =

At present the matrix contains only seventy rows, but to add a new entry is very simple. Owing to the relatively high number of conditions required, the excess of identified possible fragments is rather low.

The list of greater groups obtained in this way represents more or less the same level of information as that of the H(C) NMR groups described before. The two lists necessarily overlap giving thereby an increased chance for certain fragments to be really present.

To demonstrate the capability of the system some searches have been worked out in detail.

Examples of application

Results obtained for Structure 1 $(C_5H_8O_2)$ are shown in Table I. Only one functional group survived all the filtering steps for each ¹³C-NMR line, therefore, taking into account the environment of the carbon atoms in

Table I

Surviving functinal groups of Compound 1 through ¹³C-NMR - ¹H-NMR - IR joint interpretation

Compound 1



¹³ C-NMR lines [ppm]	Assignment	Surviving groups Inter		
177.2	(C-2)	R-COO-R	1	
74.6	(C-5)	$-C-C*H_2-O-$	1	
36.0	(C-4)	-C-C*H-C-	1	
30.4	(C-3)	$-C-C*H_2-C-$	1	
17.7	(C-6)	-C-C*H ₃ (probably AROM-C*H ₃)	1	

Joint ¹³C-NMB - ¹H-NMB - IB result

Possible structural isomers:



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* Asterisks indicate the carbon to which the chemical shift range refers

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question, two structural isomers could be constructed (Structures 1 and 2 in Table I). For the line at 17.7 ppm an additional functional group (given in parentheses) is also allowed. Groups in parentheses mean a more closely specified environment for the carbon in question; these should be considered as possible alternatives of environment. In our case the proposed aromatic environment of the methyl carbon is false, however, it is an indication of the branched nature of the carbon chain to which the methyl group is attached.

Results obtained for a somewhat larger molecule $(C_{14}H_{18}O_4)$ are given in Table II (Structure 2).

The functional groups which survived for the carbon atom at 167.0 ppm suggest the presence of a conjugated or an α -halo-substituted ester. For the carbon atom at 161.5 ppm the groups obtained are more heterogeneous: besides the conjugated ester and the -O-CO-O- group and an aromatic carbon attached to oxygen are also allowed. For carbons absorbing between 144.6 and 114.4 ppm olefinic double bonds and/or aromatic groups are proposed alternatively. These suggest the presence of a benzene ring, or olefinic double bonds, or both. Only one group survived for each of the following four lines; three of them should represent methylene carbons attached to an oxygen, and the fourth an $-O-CH_3$ group. The two proposals obtained for the last line (15.2 ppm) clearly indicate that an ethyl group should be present in the molecule.

Four of the suggested seven possible greater fragments (¹³C-NMR) are really present; one of them $(-O-CH_2-CH_3)$ is supported also by the ¹H-NMR H(C) data.

However, in this case the number of structural isomers is considerably larger.

In Structure 3 ($C_{13}H_{20}O_4$) there are identical groups arranged symmetrically (Table III). All the carbon atoms but C-4 have an intensity value of two. The possible greater fragment obtained by ¹³C-NMR indicates that the molecule should contain two identical vinyl groups and two identical $-O-CH_2-CH_3$ groups. The latter are in an ester rather than in an ether group, as indicated by the ¹H-NMR H(C) result. (The methylene carbons of the $R-O-CH_2-$ groups are not distinguished according to the nature of R in the ¹³C-NMR property matrix, but so they are in the ¹H-NMR property matrix.)

Keeping in mind these facts, only two structural isomers can be constructed (see Table III). Table II

Surviving functional groups of Compound 2 through $^{13}C-NMR - ^{1}H-NMR - IR$ joint interpretation

Compound 2



 $C_{14}H_{18}O_4$

¹³ C-NMR lines [ppm]	Assign- ment	Surviving groups	Intensity
167.0	(C-8)	$=$ C $-$ C * OO $-$ R or (CX,CONJ.) $-$ COO $-$ R	
161.5	(C-2)	=C-C*00-R or -O-C*=O-O- or 10-AROM	I-C-1 1
144.6	(C-6)	=CH	1
129.8	(C-4)	1H-AROM-C-1 or =CH-	2
127.2	(C-5)	1-C-AROM-C-1	1
115.4	(C-7)	1H-AROM-C-1 or =CH-	1
114.4 (C-3) 1H-AROM-C-1 or =CH-		2	
68.5 (C-9) – CH ₂ –O–		1	
66.5 (C-10) -CH ₂ -O-		1	
63.6	(C-11)	$-CH_2 - O -$	1
55.2	(C-1)	$-0-CH_3$	1
15.2	(C-12)	$-C-CH_2-C^*H_3 \text{ or } -O-CH_2-C^*H_2$	1
	<u>.</u>	Obtained greater fragments:	
		¹³ C-NMR	¹ H-NMR
(1) - CH = $(2) - CH_2$ (3) - O - O $(4) - CH_2$	$= CH - $ $= O - CH_3$ $CH_2 - CH_3$ $= O - CH_2$	(5) = $C - COOCH_3$ (6) = $C - COO - CH_2CH_3$ (7) one benzene ring monosubstituted**	$R-O-CH_2CH_3$

Joint ¹³C-NMR - ¹H-NMR - IR result

* Asterisks indicate the carbon to which the chemical shift range refers

** If any other carbon-carbon double bond present, this statement might be wrong

Table III

Surviving functional groups of Compound 3 through $^{13}C\text{-}NMR-^{1}H\text{-}NMR-IR$ joint interpretation

Compound 3

$$^{7}_{CH_{3}}$$
 $-^{6}_{CH_{2}}$ $-^{0}_{OC}$ $^{5}_{4}$ $^{3}_{CH_{2}}$ $-^{2}_{CH}$ $=^{1}_{CH_{2}}$
 $^{4}_{C}$ $^{6}_{CH_{2}}$ $-^{CH}$ $=^{CH_{2}}$ $^{CH_{2}}$ $-^{CH}$ $=$ CH_{2} $^{CH_{2}}$ $-^{CH}$ $=$ CH_{2} $-^{CH}$ $=$ CH_{2} $-^{CH}$ $-^{CH}$ $=$ CH_{2} $-^{CH}$ $-^{CH}$

Joint ¹³C-NMR - ¹H-NMR - IR result

C13H20

¹³ C-NMR lines [ppm]	Assignment	Surviving groups	Intensity
170.7	(C-5)	R-COO-R	2
132.5	(C-2)	=CH-	2
119.1	(C-1)	=CH ₂ -	2
61.2	(C-6)	-CH ₂ -0-	2
57.3	(C-4)	- C -	1
36.9	(C-3)	-C-C*H2-C-	2
14.1	(C-7)	$-C-C^*H_3$ (probably $-CH_2-CH_3$ or $-O-CH_2-C^*H_3$)	2

Obtained greater fragments:

¹³ C-NMR	¹ H-NMR
$\begin{array}{l} (1) - CH = CH_2 (2X)^{**} \\ (2) - O - CH_2 - CH_3 (2X) \end{array}$	$-CO-O-CH_2-CH_3$

Possible structural isomers:



* Asterisks indicate the carbon to which the chemical shift range refers ** Two identical groups

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Conclusions

The extended ASSIGNER system is capable of providing a list of functional groups that may be present in an unknown organic molecule on the basis of ¹³C-NMR, ¹H-NMR and IR spectra and the empirical formula. In addition, the program prints a list of the possible present greater fragments, too. In many cases valuable clues have been obtained in this way for the solution of structure elucidation problems. Owing to the consideration of ¹H-NMR data as an additional filtering step, the excess of possible functional groups has definitely decreased. On the average, the output of the previous version [1] contained 1.5-2.5 times more functional groups than were really present; now this ratio has been reduced to 1.6-1.9

The results obtained are promising also from the point of view of generating molecular structures.

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COMPUTERIZED CONCENTRATION RATIO DETERMINATION FOR THIN SAMPLES STUDIED BY ELECTRON MICROSCOPIC X-RAY ANALYSIS

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A simple BASIC language programme for a TPA 11/40 computer was prepared that fits a theoretical curve to the detected spectrum, calculates net X-ray intensities of elements contained in the thin specimen and finally gives atomic and weight ratios of the elements using precalculated proportionality factors. As a test of the programme microcrystal standards of known composition were analysed and weight ratios calculated.

Introduction

Electron microscopic X-ray analysis can provide an immediate correlation between the structure of a submicroscopic component of a morphologically heterogeneous sample with its chemical composition with an ultimate analytical spatial resolution of 20-30 nm, and without seriously damaging the specimen. In the case of biological specimen quantitative microanalysis has mostly been carried out on thin sections, because in addition to the advantage of a superior spatial resolution, the process of quantitation is relatively simple as compared to bulk specimen.

For the definition of "thinness" two criteria are used: 1) the electrons reach the "far" surface of the section without losing an appreciable fraction of their initial energy, and 2) the X-rays generated in the section are able to leave the section without being absorbed to an appreciable extent. In these two criteria the density through which electrons and X-rays have to pass is also significant in addition to the initial energy of the electrons. Approximately $0.5-2 \ \mu m$ thick sections of biological materials are considered thin enough to comply with these criteria.

In microanalyser systems calculating procedures for turning the measured intensities into concentrations are provided in programme packages. In these cases, however, serious programming expertise is necessary to make even minor modifications on the programmes to tailor them to particular experimental problems and these systems may be too complex compared to the

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special needs of a given laboratory. In our laboratory a BASIC language programme was prepared for a TPA 11/40 computer with 16 K core memory interfaced with an ORTEC 6230 microanalyser system. The programme makes it possible to determine concentration ratios of elements in thin sections.

The operation of the programme

The programme consists of several individual parts (independent BASIC programmes themselves) realizing the different steps of calculations and displaying the calculated spectra or their details for comparison purposes. These parts are chained together. The limited core memory of the computer made it necessary to perform the details of calculations using independent programmes, and this way it is possible to alter or replace parts of the programme very easily.

In the first part of the programme the user enters the relatively unchanging parameters and conditions — the parameters of the detector system and the accelerating voltage — and the list of elements to be considered in the analysed sample from a Table [I]. These data can be re-used until alterations are to be made. This is followed by the calculation of the proportionality factors or the so-called "relative intensities" of the elements more or less based on physical principles. The next steps are entering the spectrum from the multichannel analyser, curve fitting, calculating results for the elements and at the end displaying the results in the form of additive (generated) or subtractive (stripped) spectra or displaying the original spectrum.

The principles of the programme are similar to those of the QTHIN programme published by RUSS [2], but the structure of the programme and some of the formulas for the calculation of relative intensities are different from those used by RUSS.

X-ray production in thin samples

If the absorption and secondary fluorescence effects can be regarded as negligible, the X-ray intensity generated in a given element and the concentration of the element in the sample are in a linear relationship. Accordingly, the ratio of the concentration of two elements is:

$$\frac{C_1}{C_2} = k_{12} \frac{I_1}{I_2} \tag{1}$$

The k_{12} values can be determined from measurements on standards or can be calculated with formulas describing the generation and detection of X-rays.

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The number of characteristic X-ray quanta from the K or L electron shell of element A generated by electron excitation of a thin specimen of thickness dt can be written as:

$$\Phi_{\rm A} \,\mathrm{d}t = Q_{\rm A} \frac{N_0 C_{\rm A} \varrho}{A_{\rm A}} \, n \,\omega_{\rm A} \,\mathrm{d}t \tag{2}$$

Here Q_A is the ionization cross section of the K or L electron shell of element A; N_0 , ρ , C_A and A_A are, respectively, Avogadro's number, the sample density the concentration of A element in weight per cent, and the atomic weight of A, n is the number of electrons bombarding dt, and ω_A is the fluorescence yield of A.

The generated intensity is equal to the intensity leaving the thin specimen. The measured intensity differs from the generated intensity:

$$I_{\rm A} = \varepsilon_{\rm A} \Phi_{\rm A}$$
 (3)

where ε_A is the efficiency of response of the detector system to the X-ray from element A.

Finally, if only one peak of a given electron shell is taken into consideration during the analysis, then this I_A intensity has to be multiplied with a factor called line intensity fraction — the fraction of the peak (k_{α}) intensity in the total emission $(k_{\alpha+\beta})$. Combining these three equations we get:

$$k_{12} = rac{arepsilon_2 k_2}{arepsilon_1 k_1}, \quad ext{where} \quad k_{\mathrm{A}} = rac{Q_{\mathrm{A}} \cdot \omega_{\mathrm{A}}}{A_{\mathrm{A}}}$$
(4)

 k_{12} is the ratio of the relative intensities of elements. The X-ray generation constant k_A is independent of the detector system and may be calculated for either K or L from a set of parametrized equations at a given accelerating voltage. There has been several tentatives for the determination of these values [3, 4, 5] but at present, to our knowledge, there is no reliable Table or system of formulas available, whose results could be used without reservation for each electron shell. The measure of discrepancies is illustrated by the fact, that two authors of a summarizing collection published in 1979 [3, 4] characterized the values used in their calculations by theoretically different functions.

Calculation of relative intensities

BETHE [6] calculated the ionization cross section by using the Born approximation and we use his results in the following form:

$$Q_{\rm A} = \frac{6.51 \cdot 10^{-14} \, N_{\rm A} \, b_{\rm A}}{E_{\rm A}^2 \, U_{\rm A}} \, \ln(c_{\rm A} U_{\rm A}) \tag{5}$$

with

$$b_{\rm K} = 0.35, \quad b_{\rm L} = 0.25, \quad c_{\rm K} = c_{\rm L} = \frac{4}{1.65 + 2.35 \exp(1 - U)}$$
 (5)

according to the calculation of WORTHINGTON and TOMLIN [7]. $N_{\rm K} = 2$, $N_{\rm L} = 8$ are the number of electrons on the K or L electron shell, $E_{\rm A}$ is the critical excitation energy [8] and $U_{\rm A} = E_0/E_{\rm A}$ is the overvoltage ratio of the accelerating potential to the critical excitation energy. GOLDSTEIN *et al.* [9] sug-



Fig. 1. Relative intensities of elements for K and L electron shells

gested a relativistic correction of the accelerating potential: $E_0^x = (1 + 9.875 \times 10^{-7} E_0)E_0$ and we use this correction throughout the calculations.

The probability of X-ray emission, the fluorescence yield has been calculated by BURHOP [10] as

$$\left(\frac{\omega}{1-\omega}\right)^{1/4} = A_{\mathrm{K},\mathrm{L}} + B_{\mathrm{K},\mathrm{L}} \cdot Z + C_{\mathrm{K},\mathrm{L}} \cdot Z^3 \tag{6}$$

Here Z is the atomic number and A, B, C are constants for the excited electron shells.

The next term in the relative intensity is the detector efficiency:

$$\varepsilon_{\rm A} = \frac{\mathrm{d}\Omega}{4\pi} \,\mathrm{e}^{-\Sigma\,\mu_i l_i} (1 - \mathrm{e}^{-\mu_{si} l_{si}}) \tag{7}$$

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The i subscripts denote the absorption coefficient and thickness of the beryllium window and silicon dead layer and the si subscripts denote the same parameters for the silicon detector itself [2].

The relative intensities calculated for the K and L shells of elements with atomic number $Z \ge 11$ are summarized in Fig. 1.

Determination of concentration ratios

After the programme determined the relative intensities with the given parameters for elements specified by the user it proceeds with entering the spectrum from the multichannel analyser. As a next step it asks the user to select energies free of peaks for fitting background segments. The form of the background is $\varepsilon(E_0 - E)/E$ where ε is the spectrometer efficiency, E_0 is the accelerating voltage, E is energy. The fitting is done segmentally partly because the background fit can be done more precisely on spectrum points that are nearer to each other, partly because of the limited core memory. A practical example for such a fitted background is shown in Fig. 2a.

Elemental intensities are obtained by simultaneously fitting all of the peaks in background-subtracted spectrum segments, for each element using a least squares (matrix inversion) method. The peaks for fitting are generated using a non-Gaussian function:

$$y = e^{-0.5(x-E)^2/s_0} a_0 e^{4(x-E)} (1 - e^{0.4(x-E)^2/s_0})$$

where y is the channel height, x is the energy, E is the centroid energy and s is the peak width, $a_0 = 0.01 + 0.0025 E$ an arbitrary tailing parameter. A complete set of peak energies (3-6 for K lines, 8-12 for L lines) is needed to give proper results. These lines are also entered by the user from Tables at the beginning of the programme as part of the element list. A complete synthetic spectrum fitting a measured one (Fig. 2a) is represented in Fig. 2b.

Experimental validation of the programme

The programme was tested with microcrystal standards of known composition containing two elements whose X-rays could be detected. The standards were prepared by pipetting 0.01 M aqueous solutions of salts onto Formvar coated carbon rings. The samples were then dried at room temperature and coated with carbon in a vacuum evaporator.

The specimens were examined in a JEOL JEM 100C electron microscope using an ASID 4 D scanning attachment in transmission mode. The spectra



Fig. 2. Processing of the spectrum obtained from a KCl microcrystal. (a) Measured spectrum and calculated background segment fitted to the 1.96, 2.94, 3.48 and 3.86 keV spectral points, (b) calculated spectrum segment between 1.96 and 3.86 keV

were recorded with ORTEC 6230 energy dispersive microanalyser system. The accelerating voltage was 80 kV, the nominal beam current 30 μ A, the time of analysis 100 s. The specimen was tilted at 35° with respect to the electron beam.

Six spectra for each standard were recorded on magnetic disc and concentration ratios calculated following the measurements. The lateral dimensions of microcrystals analysed were usually less than 1 μ m. The expected and calculated concentration ratios are summarized in Table I.
Specimen	0	Exp. weight ratio	Calc. weight ratio	Deviation of calc weight ratio from exp.
NaCl	Cl : Na	1.542	1.4470 ± 0.0210	-6.16%
Na_2SO_4	S:Na	0.697	0.6300 ± 0.0110	-9.60%
$MgCl_2$	Cl : Mg	2.920	2.7920 ± 0.0170	-4.39%
$Al_2(SO_4)_3$	S:Al	1.782	1.8980 ± 0.0240	+6.26%
$\rm NH_4Al(SO_4)_2$	S:Al	2.370	2.4710 ± 0.0610	+4.26%
KCl	K : Cl	1.108	1.0972 ± 0.0048	-0.97%
K_2CrO_4	Cr : K	0.665	0.5610 ± 0.0430	-9.84%
$CaCl_2$	Ca : Cl	0.565	0.5470 ± 0.0170	-3.15%
NiCl ₂	Ni : Cl	0.828	0.8760 ± 0.0280	+5.82%
K_2SO_4	S:K	0.410	0.4400 ± 0.0100	+7.31%

 Table I

 Comparison of expected and calculated weight ratios

For the calculation of weight ratios usually intensities of K electron shells were used. The experimental results fit with the expected ratios within 10 per cent for the microcrystal standards listed in Table I. Deviations from expected weight ratios exceeded 10 per cent for $AlCl_3$ but in this case the standard error of the mean was higher than those found in Table I. In some cases intensities of L electron shells were used (Ag in Ag₂SO₄, Pb in PbSO₄, Ba in BaSO₄ and BaCl₂). BaCl₂ crystals did not prove to be stable. The elemental ratios of Ag₂SO₄ were very close to the expected. In the case of BaSO₄ and PbSO₄ the deviations were higher than ten per cent and these results were reproducible. These deviations might be caused by the choice of the numerical values for the ionization cross section Q_A .

According to the test measurements the programme works for the given analyser system using relative intensities of K shells but for L and M shells relative intensities determined by measurements on standards should be used instead of calculated ones. The programme has not been checked for any other system with different parameters, like several similar programmes described in the literature [2, 12]. In our opinion the results will be reproducible changing the terms dependent on our system in the relative intensity calculations for K electron shells or using relative intensity values determined by measurements for each electron shell. A more sophisticated fitting procedure including the physical description of the generation and detection of characteristic X-rays and white radiation, possibly in another programming language, might further improve the accuracy of intensity determination.

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STUDIES IN URANYL-SENSITIZED PHOTODECOMPOSITION OF SOME COORDINATION COMPOUNDS

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Uranyl-sensitized photodecomposition reactions of Cu-EDTA, Co-EDTA, Ni-EDTA, Cu-NTA and Fe-NTA have been studied in solid state in KBr pellet. The change have been observed by the variation in IR spectra of irradiated pellet. The use of KBr pellet as a matrix at room temperature has been established.

Introduction

The photochemistry of transition metal coordination compounds in aqueous solutions has been rather extensively investigated during the last 50 years, but relatively few investigations have been carried out on the solid state photochemical reactions of coordination compounds. These are mostly qualitative in nature [1]. Generally only the colour changes of the samples have been reported and only a few data are given on the reaction intermediates or products.

The photodecomposition of Fe(III)—DTPA complex in solid state has been studied by LAMBERT et al. [2]. Detailed examination of the IR spectra was limited to the pellet spectra in the region 1800-1500 cm⁻¹, where the antisymmetric stretching frequency of the COO group occurs. They also reported the related amounts of carbon dioxide formed after 20 minutes of ultraviolet irradiation expressed in terms of an absorption increase at 2349 cm⁻¹ using base-line technique.

Experimental

In the present work, the following complexes were prepared by the method of ALI-MARIN *et al.* [3]. Ethylenediamine tetraacetic acid complexes of copper(II), nickel(II) and cobalt(II), nitrilo triacetic acid complexes of copper(II) and iron(III).

cobalt(II), nitrilo triacetic acid complexes of copper(II) and iron(III). KBr pellets of the complexes and their mixture with uranyl nitrate were prepared keeping the M/A ratio (1000 : 1), and IR spectra were recorded on a Perkin-Elmer 377 grating

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spectrophotometer for normal sample and after irradiating the KBr pellet with ultraviolet light for various intervals of time. Different scanning speeds were applied. The prominent peaks were scanned at the lowest available speed for recording subsidiary peaks and for accurate measurements. The calibration was checked with the help of polystyrene absorption bands.

Photochemical reactions were carried out at room temperature by irradiating the pellet with UV light (300 W UV lamp kept at 7.5 cm distance from the pellet for different time periods) and then IR spectra were recorded with the pellet suspended in the light path of a Perkin-Elmer infrared spectrophotometer.

Results and Discussion

Copper(II)-EDTA complex

The H [Fe(H₂O)(EDTA)] and H₂[Fe(DTPA)] acids and their alkali salts dispersed in KBr pellets yielded CO_2 when they were irradiated with UV light [4, 5]. Similar results are expected in the photodecomposition of copper-EDTA complex in the solid state.

The IR spectrum of this complex indicates the participation of two nitrogen atoms and three carboxyl groups in the complex formation whereas the fourth carboxyl group remains uncoordinated. The presence of a band at 1730 cm^{-1} supports the presence of an uncoordinated carboxyl group in the complex.

It is interesting to note that the amount of carbon dioxide first increases upto 10 minutes followed by a decrease. There is another rise in the intensity of the band due to carbon dioxide at 2420 cm⁻¹. When the period of irradiation was increased to 40 minutes, there was a gradual decrease observable when the period of irradiation was increased further.

The first increase in the band intensity may be attributed to the formation of carbon dioxide (decarboxylation) from the uncoordinated carboxyl groups. The second decarboxylation will follow at 40 minutes and the carbon dioxide originates from the coordinated carboxyl groups.

Cobalt(II)-EDTA complex

There is no band at about 1750 cm^{-1} in the IR spectrum of cobalt(II)-EDTA complex, suggesting that all the four carboxyl groups are utilized in coordination along with the two nitrogen atoms. As there is no uncoordinated carboxyl group in this complex, one can expect decarboxylation from one coordinated carboxyl group only, in contrast to the copper(II)-EDTA complex. It is clear from the IR spectra of the irradiated pellets that carbon dioxide is formed up to 40 minutes of irradiation and then there is a gradual decrease.

Nickel(II)-EDTA complex

The absence of any band at about 1750 cm^{-1} in the IR spectrum of nickel (II)-EDTA complex indicates that EDTA acts as a hexadentate ligand in this case. As all the four carboxyl groups of EDTA are coordinated in this complex, therefore, it should behave similarly to the cobalt(II)-EDTA complex during photodecomposition in KBr pellet. This was found to be true as the IR spectra of irradiated pellets clearly indicates the decarboxylation of only one coordinated carboxyl group in nickel(II)-EDTA complex. It was of interest to note a very small amount of carbon mono-oxide formed during this photodecomposition in solid state. In this way the photodecomposition of nickel(II)-EDTA complex.

Copper(II)-NTA complex

It is expected that photodecomposition of copper(II)-NTA complex will also lead to decarboxylation, similar to copper(II)-EDTA complex. There is no uncoordinated carboxyl group in the copper(II)-NTA complex as there is no band in around 1750 cm⁻¹. It was interesting to observe that the copper (II)-NTA complex does not undergo photodecomposition, rather one coordinated carboxyl group becomes free when the period of irradiation was 60 minutes as a band develops at 1790 cm⁻¹.

The insensitized photodecomposition of copper(II)-NTA complex in solid state was also studied but no reasonable results were obtained and hence the uranyl-sensitized photodecomposition of copper(II)-NTA complex was carried out.

Iron(III)-NTA complex

In iron(III)-NTA complex also, all the three carboxyl groups of NTA are coordinated as there is no band present at about 1750 cm⁻¹. The uranyl-sensitized photodecomposition of iron(III)-NTA complex differs somewhat from that of copper(II)-NTA complex. In iron(III)-NTA complex, there is slight indication at 2100 cm⁻¹ of the formation of carbon monoxide, when the period of irradiation was 30 minutes. However, no carboxyl group was uncoordinated in this complex during photodecomposition as was in the case of copper(II)-NTA complex.

From the present work, it seems probable that this matrix technique will prove useful for quantitative and mechanism studies, not only for organic molecules but also for coordination compounds. This pellet technique has provided a simple and convenient method for investigating photochemical reactions in solid state at room temperature.

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TiCl₄-CATALYZED CONVERSION OF 1,2,3,4-TETRA-*O*-ACETYL-6-*O*-TRITYL-β-D-GLUCOPYRANOSE INTO TRIACETYLLEVO-GLUCOSAN — THE MECHANISM OF THE REACTION

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In chloroform solutions containing some alcohol, 1,2,3,4-tetra-O-acetyl-6-O-trityl- β -D-glucopyranose is transformed, on the effect of TiCl₄, into triacetyllevo-glucosan, which can be isolated in the pure state in 70% yield. The method has also been found suitable for the preparation of the tribenzoyl derivative. The conversion takes place in two steps, a rapid detritylation followed by a slower cyclization process. During detritylation, a compound of the alkoxytitanium trichloride type is formed. In the cyclization step this loses AcOTiCl₃, which formes a coordination complex with triacetyllevoglucosan in an equilibrium reaction, or an ionic complex with trityl chloride.

In continuation of our work on the elucidation of the mechanism of carbohydrate chemical reactions catalyzed by Lewis acids, the conversion of 1,2,3,4-tetra-O-acetyl-6-O-trityl- β -D-glucopyranose 1 into triacetyllevoglucosan 3 was to be investigated (Fig. 1). The practical importance of this work was, beyond the theoretical results, that compound 3 is a key material in several carbohydrate chemical reactions.

Earlier, in studies on the ring cleavage of **3** on the effect of TiCl₄ [1], the method of complex isolation was employed successfully, hence it was to be used also in the present investigations on the mechanism of the reaction. Thorough studies seemed to be necessary also in respect of the fact that BREDERECK [3] effected this conversion by means of $ZnCl_2$ and, although he assumed the formation of complexes and suggested a mechanism, did not seek to investigate the problem. Since according to our earlier experience TiCl₄ can be used more advantageously for this purpose, it was quite plausible that, if cyclization does occur also with this Lewis acid, it would provide a possibility for detailed studies of the reaction.

According to the preparative experiments, as described earlier [2], $TiCl_4$ was found to be a better catalyst than $ZnCl_2$ in this reaction; using the former agent, pure **3** was obtained in 70% yield.

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When compound 3 was mixed with equimolar $TiCl_4$ in chloroform solution at room temperature, a yellow precipitate separated immediately, which rapidly dissolved on stirring. The initial yellow colour of the reaction mixture gradually deepened during the reaction to reach deep orange. The reaction was monitored by the TLC technique and no starting material was found in a sample withdrawn after 5 min, and decomposed with water; it contained only 2, formed by detritylation. The spot of 3 appeared about 15 min later,



Fig. 1. Conversion of 1,2,3,4-tetra-O-acetyl-6-O-trityl- β -D-glucopyranose into triacetyllevoglucosan

and the conversion $2 \rightarrow 3$ took place at room temperature in about one and a half hour. These observations are indicative of a two-step reaction: rapid detritylation, followed by a slower cyclization process.

Detritylation

When a chloroform solution of the starting material was shaken with concentrated hydrochloric acid, detritylation also took place. Therefore, it was examined carefully, whether the cleavage of the trityl group occurred really on the effect of TiCl_4 , or during the decomposition of the sample with water. The sample taken from the reaction mixture of 1 and an equimolar quantity of TiCl_4 was subjected to chromatographic examination without decomposition with water, under anhydrous conditions, and it was not the starting material, either. Ten-fold dilution of the reaction mixture with CHCl_3 resulted in a slower rate of the whole conversion; the reaction time increased to 5 h, but even in this case the sample taken in the second minute did not contain any starting material.

The characteristic changes in the IR spectrum recorded immediately after combining the reagents in this delayed reaction are, as compared with

the spectrum of 1 in chloroform, the following: an intense, shifted ν CO band at 1685 cm⁻¹, beside the original ν C=O band at 1760 cm⁻¹; the ν C-C skeletal valence vibration characteristic of the trityl group is shifted from 1590 cm⁻¹ to 1585 cm⁻¹ with unchanged intensity. No change was observed in the range for ν C-O-C ether bands. In the first 20 minutes, the intensities of the characteristic bands in the spectra recorded continuously in the 1900-800 cm⁻¹ range change only slightly: the intensities of the bands at 1760, 1685 and 1070 cm⁻¹ are reduced, while that of the band at 1585 cm⁻¹ is increased.

This reaction step is still better elucidated by investigation of the complexes isolated. These complexes are summarized in Table I and are denoted by numbers. (I/serial number). The calculated amount of TrOH (the product of the hydrolysis of TrCl produced in the detritylation step) can be isolated after decomposition with water from the filtrate of the complex (I/3) separated from the reaction mixture with petroleum ether immediately after combining the reagents, and the filtrate contained no other organic substance. This definitely confirms that the instantaneous detritylation is really due to the

No	Complex	C1.9/	T; 0/	M	°C	Colour	TLC*			
140.	complex	C1 70	11 %		., .	Colour	Complex	Filtrate		
1.	$1 + \operatorname{TiCl}_4 1 : 1$	16.2	8.2	2 105-7		orange	$f 2 + { m some } f 1 \ + { m TrOH}$	TrOH		
2.	$2 + \operatorname{TiCl}_4 1: 1$	15.4	4 7.9 105-132 pale yellow		2					
3.	Separated at $t = 0 \min$	15.7	8.1	115 -	-130	yellow	2	TrOH		
4.	Separated at $t = 10 \min$	17.0	8.6	105-	-130	yellow	$2 + { m traces} { m of} \ {f 3}$	TrOH		
5.	$\begin{array}{l} \text{Separated at} \\ t=20 \ \text{min} \end{array}$	17.7	9.5	96-	-132	bright yellow	$2 + ext{some 3} \\ ext{TrOH}$	3 TrOH		
6.	Separated at $t = 30 \min$	19.5	9.7	70-	-130	orange	3 + some 2 + TrOH	$\begin{array}{c} 2 \qquad \mathbf{TrOH} \\ + \text{ some } 3 \end{array}$		
7.	Separated at $t = 60 \min$	21.1	10.0	125-	-135	bright orange	$3 + \operatorname{some}_{\mathrm{TrOH}}$	TrOH + 3		
8.	$\frac{\mathrm{TrCl} + \mathrm{TiCl}_4}{1:1}$	39.0	10.2	- 1	.65	bright orange				
	Calculated	1.TiCl	4 2	. TiCl ₄	3. Ac	OTiCl ₃	Tr+TiCl ₅	AcOTiCl ₄ ⁻ Tr ⁺		
	Cl%	18.2		26.2	2	1.2	37.8	28.8		
	Ti %		5	8.9		9.55	10.22	9.75		

Table I

Complexes isolated from the reaction of 1 and TiCl₄ (equimolar amounts, chloroform solutions at 25 $^{\circ}\mathrm{C}$)

* After aqueous decomposition

effect of TiCl_4 . The complex is, according to its analysis, not the 1 : 1 complex of the starting material and TiCl_4 ; TLC tests have shown it to be identical with 2, after decomposition.

In the IR spectrum of the complex as compared with the KBr spectrum of 1, an intense, shifted carbonyl band appears at 1680 cm⁻¹, in addition to the original $\nu C=O$ band at 1760 cm⁻¹; the corresponding $\nu_{as}C-O-C$ vibration is shifted to 1270-90 cm⁻¹ from 1215 cm⁻¹. In the range of $\nu_s C-O-C$ vibrations, the band intensity at 1070 cm⁻¹ is increased. Furthermore, a band of very small intensity appears at 1580 cm⁻¹.

For comparison, the 1:1 complex of 1 with TiCl_4 was also prepared (I/1); its composition did not agree with the calculated values. According to the TLC tests, it contained mainly 2 after decomposition, furthermore, some starting material and TrOH. It shows that compound 1 is detritylated as soon as complex formation begins. The IR spectrum of this complex is very similar to that of complex I/3.

It seemed to be interesting to prepare therefore the 1:1 complex of 2 and TiCl₄, which was expected also to react with the Lewis acid by virtue of its alcoholic hydroxyl group. Both the composition and the IR spectrum of this complex (I/2) are similar to those of the two former complexes. In the spectrum, the 3550 cm⁻¹ ν OH band has disappeared, and the formation of the C-O-Ti bond is confirmed by an inflection at 1100-1120 cm⁻¹, in agreement with literature analogues [1]. The compound of alkoxytitanium trichloride type formed from 2 is a weaker Lewis acid than TiCl₄, since the ν C=O band of the carbonyl group attached to it is found at 1680 cm⁻¹. The bathochromic shift of the carbonyl band is 80 cm⁻¹, being in good agreement with the literature data observed for the EtOTiCl₃ complex of 3 [1], and it is lower than the $\Delta\nu$ C=O shift (85-120 cm⁻¹) in TiCl₄ complexes of sugar acetates.

The intensity ratio of the original and shifted carbonyl bands in the spectrum of complex I/2 indicates the coordination of only one carbonyl oxygen atom, and this is probably the carbonyl group in 1-OAc (Fig. 2, complex *a*). This is in agreement with the monofunctional Lewis acid character of alkoxytitanium halides, mentioned in the literature. Since the complex (I/3) isolated at the beginning of the reaction is identical with this complex (I/2) on the basis of its composition as well as the IR spectrum, it can be stated that this is the complex formed also during the detritylation of 1.

The band at 1580 cm⁻¹ must be still explained. According to literature data [4], one of the most characteristic bands of the ionic $Tr^+SnCl_5^-$ complex, formed from TrCl and $SnCl_4$, can also be found here. It seemed to be advisable therefore to examine the ionic compound $Tr^+TiCl_5^-$ of similar type, formed from TrCl and TiCl₄, both in the isolated state and in chloroform solution. The isolated complex (I/8) is bright orange in colour, characteristic of com-

pounds containing Tr⁺, and its composition corresponds to the calculated values.

In the IR spectrum, the weak $\nu C_{Ar} - C_{Ar}$ doublet of TrCl at 1580/90 cm⁻¹ increased into a very intense band. In the chloroform solution of the complex the same change was observed: the $\nu C_{Ar} - C_{Ar}$ band at 1595 cm⁻¹ was shifted to 1585 cm⁻¹, and increased in intensity as a result of ion formation.

Since TrCl is formed during detritylation, this can give an ionic complex with the Lewis acid of the alkoxytitanium trichloride type present. This is indicated by the band characteristic of Tr^+ , both in the chloroform reaction



 $2 + \text{TrCl} + \text{TiCl}_4$

Fig. 2. The equilibrium developing at the beginning of the reaction between 1 and $TiCl_4$

mixture and the isolated complex. The equilibrium of the two kinds of complexes (coordination, a, ionic, b) is, however, shifted strongly to the left (Fig. 2), since the band of Tr^+ is very weak.

The equilibrium mixture of complexes a and b was to be prepared by mixing equimolar amounts of 2, TrCl and TiCl₄ in chloroform, and quenching the reaction by dilution (Fig. 2). The IR spectrum obtained in this case is similar to the solution spectrum recorded at the beginning of the reaction.

Cyclization

Further studies were focussed on the second step of the reaction, cyclization. According to the TLC tests, the spot of 3 appeared definitely after 15 min at room temperature; in the reaction delayed by tenfold dilution, this takes about 30 min. Simultaneously with the TLC tests the conversion was also monitored by the IR spectra recorded in the reaction mixture with tenfold dilution. The spectrum was recorded in the reaction mixture filled into the cell immediately after combining the reagents, and then the spectra were taken continuously in the 1900-800 cm⁻¹ range at 37 °C for 40 min. After this time, the spectrum did not change, and the TLC tests also indicated completion of the conversion $1 \rightarrow 3$.

As compared with the spectrum obtained immediately after combining the reagents, the ν C=O band shifted from 1760 cm⁻¹ to 1750 cm⁻¹, and the complex bound carbonyl band shifted from 1685 cm⁻¹ to 1665 cm⁻¹, while its intensity decreased; the intensity of the ν C_{Ar}-C_{Ar} Tr⁺ band at 1585 cm⁻¹ gradually increased. The band at 1075 cm⁻¹ slowly disappeared and simultaneously a band, probably characteristic of the 1,6-anhydro ring, developed at 1100 cm⁻¹.

The decreased intensity of the starting carbonyl band is readily explained, since the acetyl number of the product is less than that of the starting material. The decreasing intensity of the band due to the carbonyl group participating in the complex, and the increasing intensity of the Tr^+ band indicate that in the reaction mixture the amount of coordination complex is reduced, and the amount of the ionic complex is increased.

Further information on the conversion can be obtained by investigating the complexes (I/4-7) precipitated with petroleum ether from the reaction mixture at 25 °C at different times (after 10, 20, 30 and 60 min). It is worth to note the gradual deepening of the colour of these complexes, from yellow to bright orange. During precipitation with petroleum ether, the formation of two products can clearly be observed: an orange oil, which solidifies on the addition of more petroleum ether, and a yellow-coloured amorphous powder. According to TLC examination, the complex, after decomposition, contained decreasing amount of 2 and increasing amounts of 3, as well as increasing amounts of TrOH; in the filtrate of the complex, increasing amounts of 3 can be found, in addition to TrOH. The chlorine content in the complexes gradually increases, the Ti content remaining nearly unchanged.

In the IR spectra of the complexes, the change observed is similar to those found in the solution experiments: the original $\nu C=0$ band is shifted from 1760 cm⁻¹ to 1750 cm⁻¹, the complexed carbonyl band is shifted from 1680 cm⁻¹ to 1660 cm⁻¹, although with increased intensity and broadening, while the corresponding $\nu_{as}C=O=C$ band is found at 1290 cm⁻¹ instead of 1275 cm⁻¹. The $\nu C=C$ Tr⁺ band at 1580 cm⁻¹ increases simultaneously with the shifted $\nu C=0$ band. The band at 1070 cm⁻¹ slowly disappears, while a new band assigned to the anhydro ring appears at 1095 cm⁻¹; a strong, new band develops gradually at 1540 cm⁻¹.

The appearance of the band at 1540 cm⁻¹ indicates, on the basis of literature data [5], the formation of acetoxytitanium trichloride (AcOTiCl₃). In the detritylated complex, the electron-withdrawing effect, on the carbonyl oxygen is 1-OAc and the neighbouring group effect of 2-OAc results in a loosening of the C_1 -O bond and split-off of AcOTiCl₃.

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Although the split-off $AcOTiCl_3$ supports the assumption that the reaction proceeds through the coordination complex *a* of the equilibrium reaction written for the detritylation process (Fig. 2), it was to be verified that the ionic complex *b* has really no role in the further conversion. As mentioned before, when combining the reagents, 1 and TiCl₄, a complex promptly separates from the chloroform solution, but dissolves within a short time. This complex can be isolated immediately after combining the reagents and is identical with the complexes (I/1-2) prepared from 2 and TiCl₄ or 1 and



Fig. 3. Cyclization step in the conversion $1 \rightarrow 3$

 $TiCl_4$ in 1 : 1 molar ratio. Each of these complexes can be dissolved in chloroform after isolation, and the cyclization reaction takes place in the solutions at room temperature in 2 h, in the same way, as in the initial reaction mixture. Since these complexes do not contain TrCl, the TrCl remaining in the mother liquor during precipitation with petroleum ether, there is no possibility for the formation of the ionic complex; hence, cyclization takes place certainly through the coordination complex.

On this basis, the cyclization step, in which the acetoxonium ion intermediate often mentioned in the literature can also have an impotant role, can be depicted as follows (Fig. 3).

Since $AcOTiCl_3$ is a Lewis acid, it can form a coordination complex with **3**, as well as an $AcOTiCl_4^-Tr^+$ ionic complex with the TrCl present in the reaction mixture. These complexes, of course, are in equilibrium in the reaction mixture. This equilibrium is gradually shifted towards the ionic form during the reaction as shown both by the IR spectrum and the increasing chlorine content of the complexes. The increasingly intense orange colour of the complexes is another indication for this.

The 1540 cm⁻¹ band of AcOTiCl₃ is characteristic, according to the literature data, of the dimeric form [5]. The other characteristic vibration of the dimer at 1650 cm⁻¹ is overlapped by the 1660 cm⁻¹ ν C=O band, causing its broadening. AcOTiCl₃ is a stronger Lewis acid than the complex of the alkoxytitanium trichloride type formed on detritylation. Therefore, the ν C=O band in coordination shifts to lower frequencies in the complex



Fig. 4. Assumed structure of the complex $(3.\text{AcOTiCl}_3)_2$



Fig. 5. Assumed structure of the complex $(AcOTiCl_4)^2_2 - 2Tr^+$

3.AcOTiCl₃. The extent (100 cm⁻¹) of the total bathochromic shift, $\angle \nu C = O$, is as high as that caused by TiCl₄. Although in the complexes isolated the intensity of the shifted $\nu C = O$ band increases gradually, when compared with the 1 : 1 TiCl₄ complex of **3**, the carbonyl intensities indicate that in these complexes AcOTiCl₃ is attached to only one carbonyl oxygen. The hexa-covalent state of Ti is ensured by binding of the dimeric AcOTiCl₃ to carbonyl groups in two molecules of **3** (Fig. 4).

In the ionic complex (Fig. 5), dimeric $AcOTiCl_3$ develops the hexacovalent state of Ti by reacting with one molecule of TrCl each. This complex is characterized by the presence of the 1580 cm⁻¹ $\nu C_{Ar} - C_{Ar}$ band in the IR spectrum, in addition to the bands found at 1540 and 1650 cm⁻¹ ($\nu C=O$).

In the knowledge of complexes c and d the equilibrium (Fig. 6) developing at the end of the reaction can be depicted as follows:



Fig. 6. Equilibrium of the complexes formed at the end of the conversion 1 o 3

Evaluation of the results

The conversion $1 \rightarrow 3$ takes place, according to the present investigations, in two steps: a rapid detritylation is followed by a slower cyclization step. Detritylation occurs instantaneously, and takes place also under the the conditions of complex formation of 1 with TiCl₄. During detritylation a compound of the alkoxytitanium trichloride type is formed (Fig. 2, complex *a*). During cyclization, AcOTiCl₃ is released from it (Fig. 3); this forms a coordination complex with 3 and an ionic complex with TrCl in an equilibrium reaction (Fig. 6).

Extension of the cyclization reaction to other sugar derivatives and SnCl₄

Preparation of tribenzoyllevoglucosan

The conversion $1 \rightarrow 3$ can be extended to the trityl ethers of other 1,2,3,4-tetra-O-acyl- β -D-glucopyranoses. Compound 4 that is, 1,2,3,4-tetra-O-benzoyl-6-O-trityl- β -D-glucopyranose is converted into 5 on treatment with TiCl₄. The starting material of this cyclization has not been described in the literature; it was prepared on the analogy of 1 [6], that is, D-glucose was tritylated in pyridine, then acylated with benzoyl chloride [7]. The cyclization reaction was effected under the conditions given for the conversion $1 \rightarrow 3$ by refluxing the chloroform solution with equimolar amounts of TiCl₄ for 1 h, with the addition of some ethanol. The use of TiCl₄ in an increased molar ratio resulted in a higher yield (40%). Excess TiCl₄ does not interfere, since it is unable to open the ring of 5.

Conversion $1 \rightarrow 3$ on the effect of $SnCl_4$

Compound 1 can also be converted into 3 by means of $SnCl_4$. When using equimolar amounts of the starting materials in chloroform solution, the reaction takes place more slowly at room temperature than in the presence

of TiCl_4 . Also in this case, detrivulation is the faster step, but it seems to proceed only to the attainment of a certain equilibrium state. In the TLC tests, the spot of 1 disappears entirely only when the spot of 2 also disappears; that is, the detrivulation equilibrium is shifted and completed as the cyclization step proceeds. The whole reaction is slow, taking 24 h. When, however, the molar ratio of SnCl_4 is doubled, the reaction time is reduced to 5 h. The excess Lewis acid also affects the equilibrium of the detrivulation step favourably, since the spot of 1 disappears as rapidly as after 1 h.



Fig. 7. Conversion $1 \rightarrow 3$ effected by SnCl₄

When the conversion was monitored by means of the IR spectra in chloroform solution, there was observed a significant difference as compared to the reaction with TiCl_4 ; immediately after combining the reagents, a very intense Tr^+ band ($\nu C_{\text{Ar}} - C_{\text{Ar}}$) appeared at 1580 cm⁻¹, and its intensity did not change during the whole reaction. There is no separation of a complex when combining the reagents, a clear solution of magenta colour, characteristic of Tr^+ , is formed and it hardly changes later. During detritylation, probably the ionic complex b_2 is formed in an equilibrium reaction (Fig. 7).

Progress of the reaction is indicated by gradual disappearance of the band at 1080 cm⁻¹. The frequency of the original ν C=O band at 1755 cm⁻¹ remains unchanged until the end of the reaction. As the cyclization proceeds, an inflection, and later a weak band develops at 1720 cm⁻¹. Hardly any

 $\nu C = O$ band shifted can be observed. All observations indicate that in this case the complex equilibria are shifted to ionic complexes (Fig. 7).

Summarizing the results of experiments with $SnCl_4$, it can be stated that $SnCl_4$ can also be employed favourably to make 3 on the preparative scale. The end-product can be purified only by the column chromatographic technique to eliminate TrOH completely; the end-product is obtained in 60% yield when 1 is allowed to react with a double molar excess of $SnCl_4$ at room temperature for 5 h.

Experimental

IR spectra were recorded with a Perkin-Elmer 377 spectrophotometer. Decomposition temperature ranges were determined on a Büchi-Tottoli apparatus and are uncorrected. The analyses of the complexes were performed as described earlier [8]. TiCl₄ was fractionated from Cu chips; SnCl₄ was refluxed with SOCl₂ and fractionated [9]. Petroleum ether and chloroform were carefully purified and dried [8], and the latter was stabilized with 2% of dry petroleum ether [10]. The reactions, the precipitation and the preparation of the complexes were carried out in a dry box as published previously [11]. The complexes of 1 and 2 with TiCl₄ were prepared by the method described earlier [11]: a 10% solution of 1 and 2, respectively, in a 1 : 1 mixture of chloroform and petroleum ether was added to a dilute (1%) solution of TiCl₄ in petroleum ether. and the resulting complex was immediately isolated by filtration after having finished combining the two solutions, to prevent the cyclization reaction. The $1 \rightarrow 3$ conversion was effected either in solution, or by means of the complexes precipitated from the reaction mixture.

The reaction of 1 and TiCl4

(a) Compound 1 (0.7375 g; 1.25 mmole) was dissolved in chloroform (3.75 mL) and a solution of $TiCl_4$ (0.26 g; 1.47 mmole) in chloroform (0.9 mL) was added with stirring, at 25 °C; the reaction mixture was then allowed to stand at this temperature.

(b) To the reaction mixture described under (a), portions of petroleum ether (35 mL) were added at different periods in small increments; the yellow complex, which solidified on rubbing, was filtered off with suction, washed with a 1:9 mixture of chloroform and petroleum ether $(1 \times 6 \text{ mL})$, then with petroleum ether $(2 \times 6 \text{ mL})$, and dried over P_2O_5 and paraffin chips in a vacuum desiccator for 20 min. A yellow powder was obtained in 60% yield.

IR spectroscopic examination of the delayed reaction

A solution of 1 (0.3688 g; 0.625 mmole) in chloroform (1.88 mL) was mixed with a solution of TiCl₄ (0.13 g; 0.735 mmole) in chloroform (0.45 mL) at 25 °C. The complex which separated dissolved again on the effect of vigorous shaking in 30 s. An aliquot part of the reaction mixture was diluted to tenfold volume with chloroform within one minute, filled into a NaCl cell of 0.131 mm layer thickness, and the IR spectrum was continuously recorded at 25 °C or 37 °C, by means of a thermostated double-walled cell holder.

The reaction of 1 and SnCl4

(a) A solution of 1 (0.7375 g; 1.25 mmole) in chloroform (3.75 mL) was mixed with a solution of $SnCl_4$ (0.355 g; 1.36 mmole) in chloroform (0.9 mL), with stirring, at 25 °C and the reaction mixture was allowed to stand at this temperature.

IR spectroscopic examination of the reactions

The samples taken from the reaction mixtures were diluted to tenfold volume with chloroform. The IR spectra were recorded in NaCl cells of 0.131 mm layer thickness, using a reference cell of identical layer thickness filled with chloroform. The IR spectra of the solid complexes were recorded in Nujol suspensions on KBr pellets.

Thin-layer chromatographic examination of the conversion

The samples were subjected to chromatographic separtaion on plates of Kieselgel G layer of 3.5×8 cm in a 4:1 mixture of ether: petroleum ether. Detection was effected by spraying with conc. sulfuric acid and heating with an infrared lamp. In the case of 1, $R_f = 0.82$, while R_f for 3 is 0.46, and it is 0.26 for 2. Decomposition of the samples taken from the reaction mixture was effected by immediate shaking with water; the chloroform solution was dried and applied onto the layer. The complexes were also decomposed by water, the aqueous suspension was extracted with chloroform, dried after separation, and applied onto the layer.

Preparation of triacetyllevoglucosan; 3

Using TiCl4

A solution of 1 (23 g; 0.039 mole) in chloroform (115 mL) was mixed with ethanol (2.3 mL; 1.8 g; 0.039 mole), then a solution of TiCl₄ (8.63 g; 0.045 mole, 5 mL) in chloroform (27 mL) was added to it dropwise while stirring, with the exclusion of atmospheric moisture. A yellow precipitate separated and the reaction mixture became slightly warm. The precipitate dissolved rapidly on stirring. The reaction mixture was refluxed for 1 h, whereupon its colour turned into dark brown. After cooling it was poured into ice-water (300 mL), the organic phase was separated, and the aqueous solution was extracted with chloroform (3×100 mL). The combined chloroform solution was washed until neutral using water $(3 \times 100 \text{ mL}), 5\%$ NaHCO₃ solution $(2 \times 75 \text{ mL})$ and water $(2 \times 70 \text{ mL})$, dried over anhydrous Na2SO4, and clarified with activated carbon at room temperature, to obtain a yellow, clear solution. The solvent was evaporated in vacuum to leave a yellow crystalline substance (25.1 g). This was mixed with ether (35 mL) and cooled to 0 °C for 1 h. The white crystals which separated were filtered off with suction and rapidly washed with CCl_4 at 0 °C (3×7 mL). It was washed then with petroleum ether $(2 \times 10 \text{ mL})$ to obtain white crystals (8.7 g; 76.5%), m.p. 109-111 °C. After dissolution in ethanol (35 mL) white crystals were obtained (7.9 g; 70%), m.p. 110-111 °C $[\alpha_{D}^{20}]$ -59.9° (c = 2, CHCl₃).

The use of SnCl₄

A solution of 1 (7.4 g; 0.0125 mole) in chloroform (37.5 mL) was mixed with a solution of SnCl₄ (7.55 g; 0.029 mole; 3.25 mL) in chloroform (9 mL), with stirring, ensuring exclusion of atmospheric moisture. The reaction mixture became slightly warm and its colour turned immediately into deep claret. The reaction mixture was allowed to stand at room temperature for 5 h. It was then poured into water (100 mL) at 10 °C while stirring; the sticky substance which separated dissolved again on allowing the solution to warm to room temperature, and the claret colour turned into pale yellow. The aqueous phase was extracted with chloroform $(3 \times 20 \text{ mL})$, the combined chloroform solution was washed until neutral with water $(3 \times 50 \text{ mL})$, 5% NaHCO₂ (2×50 mL) and again with water (3×50 mL). It was then dried over anhydrous CaCl, and clarified with activated carbon at room temperature. The solvent was evaporated in vacuum; from the residue benzene was distilled off several times to leave an oily-solid substance (7.8 g) of yellowish-white colour. This was dissolved in benzene (15 mL) and applied onto a column packed with Silicagel 40 (60 g) in benzene; elution was effected with benzene (500 mL) and chloroform (200 mL). Evaporation of the benzene eluate yielded TrOH (2.9 g; 89%); the chloroform eluate gave, after evaporation, of the solvent, an oil (2.6 g), which solidified on standing to afford a white substance: a white powder (2.4 g; 67%) was obtained on washing with petroleum ether. After recrystallization from ethanol (10 mL), white crystals were recovered (2.15 g; 60%), m.p. 108-109 °C $[\alpha_D^{20}]$ -59.53° (c = 2, CHCl₂).

1,2,3,4-Tetra-O-henzoyl-6-O-trityl-β-D-glucopyranose; 4

Anhydrous D-glucose (18 g; 0.1 mole) and trityl chloride (30 g; 0.1 mole) were stirre in anhydrous pyridine (100 mL) at 40 °C for 15 h. The mixture was then cooled to 0 °C an freshly distilled benzoyl chloride (75.2 g; 0.54 mole; 62.2 mL) was added dropwise under stirring at 0-4 °C. After completion of the addition, the reaction mixture was stirred at this temperature for 3.5 h. It was refrigerated overnight, then water (3.2 mL) was added to decompose the benzoyl chloride; it was then diluted with chloroform (150 mL) and washed with 3N sulfuric acid (2×100 mL) and saturated NaHCO₃ solution (2×100 mL), finally dried over anhydrous Na₂SO₄. The chloroform was evaporated in vacuum to obtain a syrupy substance)94.1 g), which was dissolved in 96% ethanol (150 mL). A substance (64.1 g; 76.8%), separated

on cooling which was filtered off with suction, m.p. 99-101 °C. Since the melting point did not increase on repeated recrystallization from ethanol, the product once recrystallized from ethanol (10 mL) was dissolved in benzene (30 mL) and transferred onto a column packed with Silicagel 40 (50 g) in carbon tetrachloride, and elution followed with benzene (600 mL). The benzene was evaporated in vacuum to obtain a white powder (7.75 g), m.p. 134-135 °C. This purification procedure was repeated to give white micro crystals (6.0 g; yield of purification 77.5%); m.p. 139 °C $[\alpha_D^{20}]$ 36.00° (c = 2, CHCl₃). According to the TLC tests on Kieselgel G layers, using ether-petroleum ether 4:1 ($R_f = 0.92$) or benzene-ethyl acetate 6:0.5 ($R_f =$ = 0.68) developing solvent mixtures and detection with sulfuric acid, the substance was homogeneous.

 $C_{53}H_{42}O_{10}$ (838.915). The elemental analysis data agree with the calculated values within 0.5% error.

Tribenzoyllevoglucosan; 5

Compound 4 (3.36 g; 0.004 mole) was dissolved in chloroform (16.8 mL); ethanol (0.18 g; 0.004 mole; 0.24 mL) was added to the solution and it was mixed with a solution of TiCl₄ (1.78 g; 0.009 mole; 1.03 mL) in chloroform (4 mL), with stirring, while excluding atmospheric moisture. The reaction mixture was then refluxed for 30 min. During this period, the orange yellow colour of the solution turned into dark red. After cooling, it was poured into ice-water (60 mL) and the aqueous phase was extracted with chloroform (3 × 30 mL). The combined chloroform phases were washed with water (3 × 30 mL), 5% NaHCO₃ solution (2 × 30 mL) and again with water (2 × 30 mL) until neutral and dried over anhydrous Na₂SO₄. The solution was clarified at room temperature with activated carbon, and the solvent was evaporated in vacuum. The yellow sticky residue was mixed with ether (8 mL) the crystals which separated were cooled at 0 °C for 1 h, then filtered off with suction and washed with ether (2 × 6 mL) at 0 °C to obtain white crystals (1.2 g; 67%), m.p. 204 °C [α_{2}^{20}] -33.6° (c = 2 CHCL₃). After two recrystallizations from ethanol, 0.9 g (47.5%) of the product was obtained, m.p. 206 °C, [α_{2}^{20}] -35° (c = 2, CHCl₃). According to the TLC tests on Kieselgel G layer using benzene-ethyl acetate 6 : 0.5 developing solvent mixture and detecting with sulfuric acid, the substance was homogeneous ($R_f = 0.58$).

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STEROIDS, XXIX* NEIGHBOURING-GROUP PARTICIPATION, VI*

N-ARYLURETHANE NEIGHBOURING-GROUP PARTICIPATION IN THE 16-HYDROXYMETHYLANDROST-5-ENE-3,17-DIOL SERIES

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During alkaline methanolysis of the four possible isomers of 16-*p*-toluenesu fon y oxymethylandrost-5-ene- 3β ,17-diol-3-acetate-17-*N*-phenylurethane (1, 2, 3, 4) a cyclization reaction takes place, in which *N*-phenyltetrahydrooxazonine-2 derivatives (5a, 6a, 7a, 8a) condensed to the steroid skeleton are formed.

Thermodynamically, the *cis* isomers (**5a**, **8a**) are the more stable end-products, while the *trans* derivatives (**6a**, **7a**), formed in the kinetically controlled process, undergo ring cleavage on solvolysis to yield 16-(N-phenyl, N-methoxycarbonyl)aminomethyl derivatives (**9a**, **10a**).

Cyclization takes place through N⁻-6 N-6 neighbouring group participation.

Scort *et al.* examined the cyclization reaction of α,β - and α,γ -halogenalkyl-N-arylurethanes is alkaline media. It was found that the N-arylurethane group and its substituted derivatives reacted at different rates, depending on the inductive and conjugative effects of the substituents. The cyclization occurred typically with neighbouring-group participation, to yield N-phenyloxazolidone-2 or N-phenyltetrahydrooxazinone-2 derivatives, depending on the starting compound [1, 2].

We reported earlier that on solvolysis of the α, γ mixed *p*-toluenesulfonic-acetic esters and propionic esters of 16-hydroxymethylandrost-5-ene-3 β , 17-diol (AcO-6) or (PrO-6) neighbouring-group participation was observed in the *cis* isomers, while in the *trans* isomers such an effect could not be detected [3]. Alkaline methanolysis yielded the corresponding oxethane derivatives by (O⁻-4) (0°-4) neighbouring-group participation in the case of the *cis* isomers, whereas the *trans* isomers suffered fragmentation [4]. A similar selectivity was observed with the 16-*p*-toluenesulfonyloxymethyl-17-hydroxy derivatives, where oxidation in dimethyl sulfoxide proceeded only with the *trans* isomers, the *cis* isomers were converted into cyclic carbonates [5].

In possession of the isomer of 16-hydroxymethylandrost-5-ene- 3β ,17-diol, it seemed interesting to effect now a comparative examination of the

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solvolysis of the 16-*p*-toluenesulfonyloxymethyl-androst-5-ene-3,17-diol-3--acetate-17-*N*-phenylurethane isomers (1, 2, 3, 4).

The aim of the investigation was, on one hand, to study neighbouringgroup participation in N-phenylurethanes, and on the other, to synthesize new N-phenyltetrahydrooxazinone-2 derivatives condensed to the steroid skeleton with different ring functions.

The possible four isomers of 16-hydroxymethylandrost-5-ene- 3β ,17-diol--3-acetate [3, 6] were subjected to selective formation of the p-toluenesulfonic ester, followed by a reaction with phenyl isocyanate to obtain 16-p-toluenesulfonyloxymethylandrost-5-ene- 3β , 17-diol-3-acetate-17-N-phenylurethanes (1, 2, 3, 4). The structures were confirmed by IR and ¹H-NMR spectral data (Table I). The vNH and overlapping ester and urethane carbonyl bands appear practically at the same frequencies, that is, at 3360-3380 and 1730-1735 cm^{-1} in isomers 1, 2 and 3, respectively. In the IR spectrum of 4, the νNH and urethane carbonyl frequencies are lower (3300 and 1705 cm⁻¹, respectively), and the vNH band, which is sharp in the other three compounds, becomes broadened, indicating the formation of intermolecular hydrogen bonds developing by the participation of the urethane C=0 and NH groups. The ester carbonyl band retains the position at 1730 cm⁻¹. This association structure explains the anomalous behaviour in the ¹H-NMR spectrum observed in connection with the C-18 methyl signal. In 1 and 2, this signal appears with the usual shift value (0.85 ppm), and only a slight shift is observed also in 3 (0.75 ppm); however, in 4 these hydrogens are very strongly shielded, and the C-18 methyl signal is found at 0.25 ppm. This phenomenon can be explained by the anisotropic neighbouring-group effect of one of the phenyl rings in the substituents attached to ring D. Studies on the molecular model have shown that the N-phenyl ring in the urethane group cannot be responsible, since it cannot get close enough to the C-18 methyl group. In accordance with this, the phenomenon cannot be observed in 2 either.

When, however, this anomalous shielding is due to the phenyl ring in the C-16 tosyloxymethyl group, it should be explained why it appears only in 4. As shown by the models, the conformation favourable in this respect, that is when the *p*-methyl-phenyl ring is located close to the C-18 methyl group ("above" it), can also occur in isomer 3, since the C-18 methyl and the C-16 substituents are in β , β (cis) position. The intermolecular association in 4, verified by IR data, requires the coplanar arrangement of the urethane group and the steroid skeleton, and this means a steric arrangement of the N-phenyl group ensuring its vicinity to C-16 (s-cis). Consequently, those conformations of the tosyloxy group are sterically favoured in which the *p*-methylphenyl ring and the steroid skeleton are parallel to each other, there is s-cis arrangement, and an anomalous shielding effect occurs. This means that they have maximum statistic probability at the conformational equilibrium.

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In 3, however, free rotation of the C-16 group is not hindered, thus the probability of conformations involving strong shielding of the C-18 hydrogens is much less and, consequently, the diamagnetic shift of the C-18 methyl signal is also greatly reduced.

The preferred conformation of isomer 4 suggested above is also confirmed by the diamagnetic shift of the methylene signal in the tosyloxymethyl group. The methylene protons in compound 4 are located, in the predominating conformation, close to the N-phenyl group, above the plane of the ring, and the latter exerts a shielding effect similar to that of the tosyl ring on the C-18 methyl group.

In accordance with the configurations, the H-17 signal in compounds 1 and 4 is shifted paramagnetically, owing to the anisotropic effect of the sulfonic ester group in *cis* position.

Isomers 1-4 were subjected to methanolysis in the presence of four equivalents of NaOCH₃.

The 16α , 17α isomer (1) yielded one single end-product in a rapid reaction when refluxed for a few hours under the given experimental conditions. This product was N-phenyltetrahydrooxazinone-2 (5a) condensed to the D ring of the steroid skeleton in 16α , 17α position.

This tructure is verified by the urethane carbonyl band appearing at the same frequency as in the analogous open-chain compound (in the spectra of **5a**, **b**-**8a**, **b** it was found at 1710 and 1690, in **7a** at 1675 cm⁻¹), furthermore, in the ¹H-NMR spectrum the signal of the $-NCH_2-$ group was found and could be clearly identified in the shift range expected, in all cases. The hydrogens of this group coupled with the H-16 atom form the AB part of an ABX spin system, consequently they produce a multiplet consisting of 8 lines.

The cyclization reaction can be explained by a nucleophilic attack by the nitrogen atom of the deprotonated acid amide. The groups participating in the reaction are located on the same side in space, opposite to the C-18 methyl group, in a particularly favourable position in respect of both the cyclization reaction and the stability of the resulting ring system.

Isomer 16β , 17β (4) is also converted in a rapid reaction into the corresponding heterocyclic compound (8a) condensed in 16β , 17β position, as shown by the analogous IR and NMR spectral data (Table I). The heterocycle formed in this case is sterically more hindered than in 5a, since it is located on the same side as the C-18 methyl group. In spite of this, neither 5a nor 8a is decomposed on the effect of excess NaOCH₃ when refluxed for 48 h (Fig. 1).

In the case of the two *trans* isomers $(16\alpha, 17\beta(2); 16\beta, 17\alpha(3))$ the occurrence of cyclization was also established, in spite of the fact that in former studies on reactions involving neighbouring-group participation, the formation of cyclic compounds from *trans* isomers was not observed [3, 4]. Acta Chim. Acad. Sci. Hung 111, 1982

¹ H-NMR and IR data compounds 1-4 and 5a, b-	10a , b (δ _{TMS} = 0 ppm,	CDCl_3 and $\text{DMSO-}d_6$; cm ⁻¹ , KBr pellets)
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			SCH ₃		ðCH2	δH-17	ðН-3	ðH-6	ðNH		ðArH	
	18	19	Ac	Ts'OMe	d(2H)	đ	$\Delta \nu = 25 \text{ Hz}$	$\Delta v = 4.8 \text{ Hz}$	broad	Ph: s(5H)	$T_8 \times : H-3.5$	H-2,6
1	0.85	1.05	2.05	2.35	4.10°	4.95°	\sim 4.6	5.35	${\sim}6.7$	\sim 7.2	\sim 7.3	\sim 7.7
2	0.85	1.02	2.05	2.40	\sim 4.1°	4.45^{+}	\sim 4.6	5.40	${\sim}6.7$	\sim 7.3Ø	\sim 7.3Ø	7.75
3	0.75	1.00	20.0	2.40	\sim 4.2°	4.50	\sim 4.5*	5.35	${\sim}6.7$	7.35	\sim 7.3	7.75
4	0.25	0.95	2.00	3.70°	3.70°	4.70^{+}	\sim 4.5*	5.35	${\sim}10.6$	7.40	\sim 7.2	7.75
5a	0.90	1.10	-	-	$\begin{array}{c} 3.95\\ 3.40\end{array}$	4.35°	\sim 3.5*	5.35		7.30	—	-
5b	0.85	1.05	2.05		3.90 3.40	4.35°	\sim 3.6	5.35		\sim 7.3	_	
6a	1.00	1.05	-	-	${\scriptstyle \sim3.4\ \sim3.7}$	3.75+	\sim 3.6	5.35	-	7.30	-	-
6b	1.00	1.08	2.03		${\scriptstyle \sim3.5\ \sim3.7}$	3.80^{+}	\sim 4.6	5.35		7.30	—	
7a	1.05	1.10		-	\sim 3.5	3.95^{+}	\sim 3.5	5.3	-	7.30	—	-
7b	1.00	1.10	2.00	_	\sim 3.5	3.95^{+}	\sim 4.6	5.35		7.30	-	-
8a	0.98	1.03	—	-	$3.55 \\ 3.70$	4.30^{+}	\sim 3.6*	5.35	-	7.25	—	-
8b	0.95	1.05	2.00		${\sim}3.5\ {\sim}3.7$	4.30+	\sim 4.5	5.35		\sim 7.3	_	-
9a	0.75	1.00	-	3.65	3.90°	$\sim 3.4^{\circ}$	\sim 3.6	5.35	_	\sim 7.3	-	-
9b	0.75	1.00	2.05	3.70	\sim 3.8°	4.65	\sim 4.6*	5.40	-	\sim 7.4	-	-
10a	0.70	1.00		3.65	3.80°	3.30°	\sim 3.5*	5.30	-	\sim 7.3		-
10b	0.90	1.00	2.00 2.05	3.70	\sim 3.9	4.70	\sim 4.6*	5.40	-	7.35	-	-

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vNH/vOH νSO_2 bands vC=0 βNH vC-0/vC-N band $\gamma C_{Ar} H / \gamma C_{Ar} C_{Ar} bands$ (tosyl, phenyl) bands bands band (ester, urethane) 1 3360 s 1735 1360, 1175, 955, 560 1540 1245, 1220 815, 765, 695, 665 3380 s 1735 2 1340, 1175, 940, 580 1535 1255. 1225 820, 810, 765, 755, 690, 675 3380 s 1730 3 1350, 1170, 940, 565 1540 1260, 1230 835, 810, 770, 750, 690, 670 3300 b 1705 1420, 1190, 1180, 980. 1545 1275, 1245 815, 760, 695 4 1730* 960. 595. 560 1410, 1150, 1060 3600 - 32001710 760, 700 5a 1735* 1410, 1250, 115, 1030 760, 700, 695, 680 5b 1695 3600 - 33001690 1425, 1165, 1076, 1050 6a 770, 760, 710, 700 \sim 3500 \otimes 1690 1420, 1250, 1170, 1155, 760 1740* 1035 3490 1675 1430, 1160, 1150, 1065. 6c 770, 695 1060 1690 1250, 1160, 1145, 1030 7a 770, 695 1735* 1690 1410, 1170, 1160, 1085, 7b 3470 780, 765, 695 1070.1030 1710 1410, 1260, 1160, 1090. 8a 775, 760, 700 1725* 1035 **8**b 3600 - 32001690 1050, 1030 765, 750, 695 $1740 \times$ 9a ${\sim}3430^{\,\otimes}$ 1700 1245, 1030 765, 750, 695 1725*1685 **9b** 3600 - 32001300, 1050 770, 755, 695 10a ${\sim}3425^{\,\otimes}$ 1690 1240, 1210, 1030 750, 695 1720* 10b

Table I (continued)

 $^{\circ}(J = 6-7 \text{ Hz}) \bullet (J = 3 \text{ Hz}) + (J = 9.20 \text{ Hz})$, *overlapped signal, $^{\varnothing}$ coincident signals $^{\times}AA' BB'$ multiplet (2×2H), J_{AB} 9 Hz $^{\otimes}$ main maximum of the broad absorption

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The cyclic compounds formed in these cases, however, are unstable, and undergo further methanolysis with ring cleavage to give end-products of the 16-(N-phenyl, N-methoxycarbonyl)aminomethyl type (9a, 10a).

This was indicated by the presence of ν OH and urethane carbonyl bands in the IR spectra of 9a and 10a, and the appearance of ester bands instead of the former bands in the IR spectra of 9b and 10b; further evidence is that the signal of the methoxyl group is found in the ¹H-NMR spectra of all the four compounds.

Two hypotheses can be forwarded to explain the cyclization reaction of the *trans* isomers (2, 3).

On the basis of literature observations [7], it can be assumed that during solvolysis enlargement of the D ring in the steroid skeleton takes place involving the participation of the 16-*p*-toluenesulfonyloxymethyl group to yield an N-phenyloxazolidone-2 condensed to the D-homo ring, which undergoes ring cleavage under the solvolysis conditions (Figs 2 and 3, Path 1). This hypothesis is supported by the facts that in this way a *cis*-fused Nphenyloxazolidone-2 ring can develop, furthermore, the cleavage of rings of this type has been reported earlier [8].

This assumption was not confirmed, however, by the spectral data. If the assumed oxazolidone ring were present, the $\nu C=0$ band should appear. at a frequency much higher than the observed value (1750-1730 cm⁻¹)

In the ¹H-NMR spectrum the oxazolidone structure condensed with a six-membered ring D would produce not only an NCH signal with an intensity equivalent to one proton, but also a more complex structure consisting of at least 16 lines.

In the other hypothesis, *trans*-fused N-phenyltetrahydrooxazinone-2 rings (**6a**, **7a**) are formed in a kinetically controlled process on the effect of the strongly nucleophilic nitrogen atom. The structure developed in this manner is, however, unstable; the heterocycle is split under the conditions of the solvolysis to yield the corresponding 16-(N-phenyl, N-methoxycarbonyl)-aminomethylandrost--5-ene- 3β ,17-diols (**9a**, **10a**) (Figs 2 and 3, Path 2).

In the case of N-arylurethanes examined by us, the neighbouring-group participation is not stereospecific. The strongly nucleophilic acid amide nitrogen atom causes cyclization in both the cis (1, 4) and the trans (2, 3) isomers. The cyclic cis products are stable (5a, 8a) whereas the trans-fused rings (6a, 7a) undergo ring cleavage during solvolysis.

The ring cleavage process yielding N-phenyl, N-methoxycarbonyl- α , γ -aminoalcohols is anomalous. N-Aryl- and N-alkyltetrahydrooxazinone-2 systems described in the literature usually decompose into N-aryl- and N-alkylaminoalcohols under solvolytic conditions [9, 10].

The cyclization reaction takes place through a neighbouring-group participation of type N⁻-6 N-6 [1].

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No	Formula	M.p., °C	[.].	P.	Analysis,	% Calcd	./Found	Method	
190.	Molecular weight	crystallization	[α]D	Γ _f	С	н	N	Method	
1	$\substack{\mathrm{C}_{36}\mathrm{H}_{45}\mathrm{O}_{7}\mathrm{SN}\\635.83}$	175–177 Methanol	+ 8	0.7 (I)	80.69 80.52	$\begin{array}{c} 8.46\\ 8.57\end{array}$	$\begin{array}{c} 2.61 \\ 2.35 \end{array}$	1	
2	$\substack{\mathrm{C_{36}H_{45}O_7SN}\\635.83}$	203-204 Methanol	- 56	0.65 (I)	$\begin{array}{c} 80.69\\ 80.45\end{array}$	8.46 8.35	$\begin{array}{c} \textbf{2.61} \\ \textbf{2.50} \end{array}$	1	
3	$\substack{\mathrm{C}_{36}\mathrm{H}_{45}\mathrm{O}_{7}\mathrm{SN}\\635.83}$	193—195 Benzene-petroleum ether	+ 26	0.65 (I)	80.69 80.55	8.46 8.37	$\begin{array}{c} 2.61 \\ 2.52 \end{array}$	1	
4	$\substack{\mathrm{C_{36}H_{45}O_7SN}\\635.83}$	Oil	- 13	0.7 (I)	80.69 80.65	$\begin{array}{r} 8.46\\ 8.30\end{array}$	$\begin{array}{c} 2.61 \\ 2.50 \end{array}$	1	
5a	$\substack{\mathrm{C}_{27}\mathrm{H}_{25}\mathrm{O}_{3}\mathrm{N}\\421.58}$	242-244 Chloroform- petroleum ether	- 63	0.6 (II)	$\begin{array}{c} 76.92 \\ 76.80 \end{array}$	$\begin{array}{c} 8.36\\ 8.21\end{array}$	$\begin{array}{c} 2.32\\ 3.50\end{array}$	2	
5b	$\substack{\mathrm{C}_{29}\mathrm{H}_{37}\mathrm{O}_4\mathrm{N}\\463.62}$	204–205 Benzene– petroleum ether	- 89	0.9 (II)	$\begin{array}{c} 75.13 \\ 75.30 \end{array}$	$\begin{array}{c} 8.04\\ 8.15\end{array}$	$\begin{array}{c} 3.02\\ 3.18\end{array}$	3	
6a	$\substack{\mathrm{C}_{27}\mathrm{H}_{35}\mathrm{O}_{3}\mathrm{N}\\421.58}$	158—161 Chloroform- petroleum ether	+ 57	0.5 (II)	$\begin{array}{c} 75.92 \\ 76.70 \end{array}$	8.36 8.20	$\begin{array}{c} 3.32\\ 3.45\end{array}$	2	
6b	$\substack{\mathrm{C_{29}H_{37}O_4N}\\463.62}$	268–269 Chloroform– petroleum ether	+ 45	0.85 (II)	$\begin{array}{c} 75.13\\ 75.30\end{array}$	$\begin{array}{c} 8.04\\ 8.22\end{array}$	$\begin{array}{c} 3.02\\ 3.35\end{array}$	3	
7a	$\substack{\text{C}_{27}\text{H}_{35}\text{O}_3\text{N}\\421.58}$	318-320 Chloroform- petroleum ether	-134	0.4 (II)	$\begin{array}{c} 76.92\\ 76.80 \end{array}$	8.36 8.49	$\begin{array}{c} 3.32\\ 3.50\end{array}$	2	
7b	$\substack{C_{29}H_{37}O_4N\\463.62}$	282–284 Chloroform– petroleum ether	-133	0.8 (II)	$\begin{array}{c} 75.13\\ 75.05\end{array}$	$\begin{array}{c} 8.04\\ 8.16\end{array}$	$\begin{array}{c} 3.02\\ 3.45\end{array}$	3	
8a	$\substack{\text{C}_{27}\text{H}_{35}\text{O}_{3}\text{N}\\421.58}$	196–200 Benzene- petroleum ether	+ 5	0.55 (II)	$\begin{array}{c} 76.92 \\ 76.82 \end{array}$	$\substack{8.36\\8.27}$	$\begin{array}{c} 3.32\\ 3.51 \end{array}$	2	
8b	$\substack{\mathrm{C}_{29}\mathrm{H}_{37}\mathrm{O}_4\mathrm{N}\\463.62}$	236–238 Chloroform– petroleum ether	- 18	0.9 (II)	$\begin{array}{c} 75.13\\ 75.20\end{array}$	$\begin{array}{c} 8.04\\ 8.16\end{array}$	$\begin{array}{c} 3.02\\ 3.34\end{array}$	3	
9a	$\substack{C_{28}H_{36}O_4N\\450.60}$	199 Benzene– petroleum ether	- 71	0.35 (II)	$\begin{array}{c} 74.63\\74.51 \end{array}$	$\begin{array}{c} 8.05\\ 8.27\end{array}$	$\begin{array}{c} 3.10\\ 3.45\end{array}$		
9b	$\substack{\mathrm{C}_{32}\mathrm{H}_{43}\mathrm{O}_{6}\mathrm{N}\\537.70}$	163—165 Methanol	- 26	0.45 (I)	$\begin{array}{c} 71.48\\71.30\end{array}$	$\begin{array}{c} 8.06\\ 8.17\end{array}$	$\begin{array}{c} 2.60\\ 2.70\end{array}$		
10a	$\substack{C_{28}H_{36}O_4N\\450.60}$	188—191 Benzene- petroleum ether	— 55	0.3 (II)	$\begin{array}{c} 74.63\\74.43\end{array}$	$\begin{array}{c} 8.05\\ 8.19\end{array}$	$\begin{array}{c} 3.10\\ 3.18\end{array}$		
10b	$\substack{\mathrm{C}_{32}\mathrm{H}_{43}\mathrm{O}_{6}\mathrm{N}\\537.70}$	170-172 Methanol	— 39	0.4 (I)	$\begin{array}{c} 71.48\\ 71.58\end{array}$	$\begin{array}{c} 8.06\\ 8.35\end{array}$	$\begin{array}{c} 2.60\\ 2.77\end{array}$		

Table II

(I) Methanol : benzene (1 : 99)(II) Methanol : benzene (5 : 95)

Experimental

M.p.'s were measured on a Kofler block and are uncorrected.

Specific rotations were determined with a Polamat-A polarimeter.

The ¹H-NMR spectra were recorded with a Varian EM-360, EM-390 and a Jeol HL-60 spectrometer at room temperature in CDCl_3 and $\text{DMSO-}d_6$ solutions, using TMS as internal standard.

The IR spectra were obtained with Perkin-Elmer 325 and 577 spectrophotometers in KBr pellets.

The thin-layer chromatograms were prepared on Kieselgel-G (Merck) layers of 0.5 mm thickness. The developing solvent systems were the following: (I) methanol : benzene (1 : 99); (II) methanol : benzene (5 : 95). Detection was effected by spraying with 50% aqueous phosphoric acid and subsequent heating at 100-120 °C for 15 min. The R_f values were determined in UV light of 365 nm wave length.

In the column chromatographic separation procedures Al_2O_3 of activity III-IV standardized according to Brockmann was used. Dimensions of the chromatographic columns were: 25 cm length 2 cm diameter; weight of Al_2O_3 packing: 50 g.

16-p-Toluenesulfonyloxymethylandrost-5-ene-3β,17-diol-3-acetate-17-N-phenylurethane (1, 2, 3, 4)

(General procdure No. 1)

4

16-p-Toluenesulfonyloxymethylandrost-5-ene- 3β ,17-diol-3-acetate [3, 6] (2.58 g; 0.005 mol) was dissolved in dichloromethane (30 mL), mixed with phenyl isocyanate (2.4 g; 0.02 mole) and triethylamine catalyst (0.5 mL), and heated at the temperature of boiling for 6 h. The reaction mixture was then poured into 10% NaHCO₃ solution, the dichloromethane fraction was washed thoroughly with water, dried, and evaporated to dryness. The residue was subjected to chromatographic separation in a mixture of benzene and petroleum ether (50 : 50).

 5×100 mL of benzene : petroleum ether (50 : 50) removed the polymeric contaminants; 5×100 mL of benzene eluted the desired end-product of high purity.

N'-Phenyl-3 β -hydroxyandrost-5-ene-[16,17-e]-4H-oxazine-2'-one (5a 6a, 7a, 8a)

(General procdure No. 2)

Compound 1, 2, 3, or 4 (3.17 g; 0.005 mol) was dissolved in methanol (30 mL), mixed with NaOCH₃ (1.08 g; 0.02 mol) and maintained the temperature of boiling. The progress of the reaction was monitored by TLC. In the preparation of 5a and 8a, refluxing was continued until the starting compounds (1 and 4) had been used up. In the preparation of 6a and 7a, the conversion was allowed to run until the appearance of 9a and 10a.

The reaction mixture was neutralized with dilute hydrochloric acid, diluted with water, the crystals which separated were filtered off, dried and recrystallized from a mixture of chloroform and petroleum ether, or chloroform and benzene.

N'-Phenyl-3\beta-acetoxyandrost-5-ene-[16,17-e]-4H-oxazine-2'-one (5b, 6b, 7b, 8b)

(General procedure No. 3)

Compound 5a, 6a, 7a, or 8a (0.42 g; 0.001 mol) was dissolved in a mixture of pyridine and acetic anhydride (1:1) (3 mL), allowed to stand overnight, and then diluted with water. The precipitate which separated was filtered off, washed thoroughly with water and crystallized from methanol.

16α -(N-Phenyl, N-methoxycarbonyl) aminomethylandrost-5-ene- 3β , 17β -diol (9a)

Compound 2 (3.17 g; 0.005 mol) was dissolved in methanol (30 mL) and refluxed with NaOCH₃ (10.8 g; 0.02 mol) for 6 h. The reaction mixture was neutralized with dilute hydrochloric acid, the crystals which separated were filtered off, dried and crystallized from a mixture of benzene and petroleum ether (1.85 g; 82.2%).

16α -(N-Phenyl, N-methoxycarbonyl) aminomethylandrost-5-ene- 3β , 17β -diol--3,17-diacetate (9b)

Compound 9a (0.450 g; 0.001 mol) was dissolved in a mixture of pyridine and acetic anhydride (1:1) (2 mL), allowed to stand overnight, and then diluted with water. The precipitate which separated was filtered off and recrystallized from methanol (0.51 g; 94.9%).

16_β-(N-Phenyl, N-methoxycarbonyl)-aminomethylandrost-5-ene-3_β,17_α-diol (10a)

Compound 3 (3.17 g; 0.005 mol) was processed as given for 9a, but with a reaction time increased to 18 h (1.62 g, 72%).

168-(N-Phenyl, N-methoxycarbonyl)aminomethylandrost-5-ene-38,17a,3,17--diacetate (10b)

Compound 10a (0.450 g; 0.001 mol) was acetylated as given for 9b (0.500 g; 93.1%).

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CROWN ETHERS INCORPORATING SUGAR UNITS, III

PREPARATION OF BIS-GLUCOPYRANOSIDO- AND BIS-GALACTO-PYRANOSIDO-CROWN ETHERS AND STUDIES ON THEIR COMPLEX-FORMING PROPERTIES

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In a biphase system formed from tetrahydrofuran and concentrated KOH solution, the 18-membered crown ethers, 5, 7, containing galactopyranoside units, and 24-membered ones, 9, containing glucopyranoside units have been prepared. The association constants (K_a) of these compounds with Li, Na, K and NH₄ cations were measured. These were found to decrease in the order $K^+ > NH_4^+ > Na^+ > Li^+$. With all cations, the highest K_a value was obtained with the crown compounds containing *bis*-galactoside. Some hydroxy, acetyl and tosyl derivatives of bis-glucopyranosido-18-crown-6 (3a) were also prepared.

As reported earlier [1, 2], a new method has been elaborated for the preparation of sugar-based crown ethers. The method is based on the reaction of, e.g., methyl-4,6-O-benzylidene- α -D-glucopyranoside (1) with diethylenegly-col ditosylate (2) in the biphase system formed from tetrahydrofuran or dioxan and 50% potassium hydroxide solution, to obtain the *bis* (methyl-4,6-O-benzylidene- α -D-glucopyranosido)-18-crown-6 isomers (3).

In the present paper and extension of this reaction to the preparation of *bis*-galactopyranosido-18-crown-6 and *bis*-glucopyranosido-24-crown-8 compounds is reported, investigations on their complex-forming ability are described, furthermore, synthesis of various derivatives obtained from *bis*glucopyranosido-18-crown-6 (**3a**), prepared earlier, are given.

Results and Discussion

Extension of the synthesis effected in the biphase system

The reactions were effected with various starting materials; different sugar components and different oligoethylene ditosylates were used in the reactions.

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In this way, methyl-4,6-O-benzylidene- α -D-galactopyranoside (4) yielded compound (5), methyl-4,6-O-benzylidene- β -D-galactopyranoside (6) gave the crown compound 7; in both cases mixtures of the *cis* and *trans* isomers were obtained in the reaction with 2. The yields for 5 and 7 were 15% and 28%, respectively. In contrast with the crown ether containing the glucopyranoside unit (3), compound 5 is soluble not only in chlorinated solvents, but also in alcohol. It is to be noted that crown compounds 5a and 5b have been prepared earlier by SCHRÖDER *et al.* by a different procedure [3].

The reaction of 1 and triethyleneglycol ditosylate (8) gave bis-glucopyranosido-24-crown-8 (9) in 16% yield. This compound is well soluble in the majority of organic solvents, except for ether and petroleum ether.

Compounds 5, 7 and 9 were identified by elemental analysis, IR and ¹H-NMR, furthermore, by mass spectrometry. All these investigations, however, failed in making possible the distinction and identification of the *cis* and *trans* isomers (a and b). The isomers of 3, described earlier, were identified by X-ray crystallography [4]. The isomers of 5 (a and b) were separated, but in lack of suitable crystals, no such examination could be effected. STODDART *et al.* [5] determind the steric structures, of complexes of compounds prepared by the NaH/DMSO cyclization method by means of the dynamic NMR technique, thus the structures of the *cis* and *trans* isomers of 5 were rendered probable by comparing the melting point and rotation values. It is to be noted here that the complexing ability of the *cis* and *trans* isomers does not differ significantly, therefore in studies on complex-forming properties the mixture of isomers may also be used.

Complex formation

The complexing ability was investigated on some alkali metals (Li, Na, K and ammonium picrate in chloroform by the UV technique, using the method suggested by CRAM *et al.* [6].

The association constant K_a was calculated according to Eq. (1):

$$K_{
m a} = rac{R}{(1-R) \, K_{
m d} \{ [K {
m Pic}]_{
m H_2O} - R[C]_{
m CHCl_3} (V_{
m CHCl_3} / V_{
m H_2O}) \}^2}$$
(1)

where

$$\mathbf{K}_{d} = \frac{[\mathbf{K}^{+} \mathbf{Pic}^{-}]_{CHCl_{s}}}{[\mathbf{K}^{+}]_{H_{s}O} \cdot [\mathbf{Pic}^{-}]_{H_{s}O}}$$
(2)

 $K_{\rm d}$ = distribution of the metal picrate in the chloroform-water system, calculated according to Eq. (2); R = X/Y; X = mole picrate in the chloroform phase; Y = mole crown compound in the chloroform phase; $[K {\rm Pic}]_{{\rm H}_2{\rm O}}$ = concentration of the metal picrate in the aqueous phase before complex formation; $[C]_{\rm CHCl_3}$ = concentration of the crown compound in the chloroform phase; $V_{\rm CHCl_3}$ = volume of the chloroform phase (cm³); $V_{\rm H_2{\rm O}}$ = volume of the aqueous phase (cm³). In the case of water-soluble crown compounds, the partition of the crown compound between the aqueous and chloroform phases under the conditions of complex formation was measured and considered in calculating $K_{\rm a}$. Table I shows the log $K_{\rm a}$ values for crown compounds carrying

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	a	101	C	

Association cons	stants of crown	i compounds	$(\log K)$	(a) in	chloroform	at	22 °	0
				C1 /				_

Start an augus designation	Crown compd.			$\log K_{i}$		
Start ng sugar derivative	compd.	Li+	Na+	K+	\mathbf{NH}^+	K+(CDCl ₃)
Methyl-4.6-O-benzylidene-a-D-gluco-	3a	3.99	3.95	4.93	4.06	4.87
Methyl-4,0-0-benzylidene-&-D-gluco- pyranoside Methyl-4,6-0-benzylidene-&-D-galacto- pyranoside	3b	4.14	4.05	5.04	4.12	4.95
Methyl-4,6-O-benzylidene-a-D-galacto-	5a	4.02	4.22	6.61	5.15	6.11
pyranoside	5b	4.13	3.28	6.12	5.20	-
Methyl-4,6-O-benzylidene-β-D-galacto- pyranoside	7a + 7b	4.17	4.73	6.46	5.53	6.34
Methyl-4,6-O-benzylidene-α-D-gluco- pyranoside	9a + 9b	3.68	3.73	5.46	4.59	5.46
Dibenzo-18-crown-6	10	4.08	4.44	7.85	5.96	7.55

protective groups on the sugar unit and, for comparison, those of dibenzo-18--crown-6 (10) available commercially.

It is found that the complex stabilities of the 18- and 24-membered crown ethers shown in the Table decrease in the order $\rm K^+ > \rm NH_4^+ > \rm Na^+ > > \rm Li^+$.

For the lithium ion, the inner space in the 18- and 24-membered rings is far too large; the cation is far from the oxygen donor atoms and even farther from the oxygens of the annellated units, hence the latter have practically no influence. This is supported by the practically identical complexing properties of compounds 3, 5, 7 and 10 (log $K_a = 3.99 - 4.17$) and by the even lower value (log $K_a = 3.68$) for the 24-membered compound (9). A similar statement can be made about the complex formation with Na⁺, having a larger ionic diameter; here, however, a slight effect of the various sugar components can also be observed, thus the complexing ability of 7, containing galactoside, is stronger than that of 3, containing glucoside. The association constants measured with K^+ and NH_4^+ ions are significantly higher. The ionic diameter of K^+ corresponds to the inner dimensions of the 18-crown-6 ring [7, 8], thus it can approach the crown ring oxygens and the sugar units participating in the constitution of the crown, and the latter have now a more pronounced effect on the stability of the resulting complex. Hence the complex formation constants of crown compounds 5a, 5b and 7, containing galactopyranoside, is by one, or one-and-a-half order of magnitude higher in complexes formed with K^+ , and also with NH_4^+ having similar dimensions ions, than those of crowns 3a and 3b, containing glucopyranoside units. A similar tendency was observed by STODDART et al. [5] when measuring the stability of the complexes of 3 and 5 formed with t-butylammonium thiocyanate, by another method.

The configuration of the glucosidic linkage affects complex formation less; the β -anomer of 7 gives a somewhat more stable complex than the α -anomer of 5 does.

The association constants of the *cis* and *trans* sugar crowns are, as it has been mentioned, almost identical, as shown by the corresponding values for **3a** and **3b** and **5a**.

The 24-membered crown compound also forms a significantly stronger complex with the K^+ ion than with the Li^+ or Na^+ ion; this can be explained by the higher flexibility of the larger ring, the K^+ ion is "wrapped up" by the crown ring.

Comparing the complex formation constants measured with the K^+ ion and the NH⁺ ion having similar dimensions, the latter are found to be lower by about one order of magnitude. This tendency has been observed in other crown compounds, too.

Comparison of the association constants measured with K^+ ions in sugar crowns and dibenzo-18-crown-6 has shown that the latter value is higher
by one or two orders of magnitude. This can be due to the differences in the rigidity and solvation ability of the molecules.

Finally, the values shown in the last column in Table I confirm that in the determination of the association constants chloroform can also be used instead of CDCl_3 employed in certain works [6].

Synthesis of the derivatives of bis-glucopyranosido-18-crown-6 (3a)

It was described earlier [1, 2] that crown compounds of various solubility had been prepared by removing the protective groups of **3b** and applying acylating reactions. Now the derivatives of **3a** were obtained in a similar manner (Fig. 1). Compound **3a** was refluxed with 2N hydrochloric acid to split off **t**he methyl and benzylidene groups, which occurred in 8 h. The resulting crown compound **11** is soluble in water, methanol and ethanol, and insoluble in chlorinated solvents. Selective removal of the benzylidene groups was effected by the method suggested by JEANLOZ [9]: **3a** was heated with glacial acetic acid to obtain the tetrahydroxy crown compound **12**; this is soluble



Fig. 1

again only in water and alcohols. The trans isomer prepared from **3b** [2] is soluble in chloroform and dichloromethane. Compound 12 was allowed to react with acetic anhydride in pyridine to yield the tetraacetyl derivative 13, which is soluble in both alcohol and chloroform.

The tetrahydroxy crown compound 12 was allowed then to react with p-toluenesulfonyl chloride (2.1 mol) in pyridine at room temperature to obtain the ditosyl derivative 14, which is also well soluble in alcohol and chlorinated solvents. On the effect of acylation the singlet characteristic of OCH₃ protons appears at $\delta = 3.32$ ppm in CDCl₃ in the ¹H-NMR spectrum. Tosylation took place selectively: only the primary hydroxyl groups are acylated. This is shown by the doublet appearing at $\delta = 4.22$ ppm belonging to the C₆-H protons, in the ¹H-NMR spectrum of 14.

Experimental

M.p.'s were measured with a Büchi 510 apparatus and are uncorrected. The IR spectra were recorded with a Perkin-Elmer 237 and a Spectromom 2000 instrument in KBr pellets, the ¹H-NMR spectra were obtained with a Perkin-Elmer R12 (60 MHz) instrument using TMS internal standard. Mass spectra were measured with a Jeol JMS-01 SG-2 instrument, the UV spectra were determined with a Hitachi-Perkin-Elmer 124 spectrometer; elemental analysis data were obtained with a Perkin-Elmer 240 automatic analyser.

Determination of the association constants

Two centrifuge tubes of 10 cm³ volume were equipped with magnetic stirrers. In one of the tubes, 0.015 mol/dm³ aqueous picrate solution (0.5 cm³), in the other tube distilled water (1 cm³) were placed, then a 0.075 mol/dm³ chloroform solution (0.2 cm³) of the crown compound examined was added to both tubes. The closed tubes were centrifuged shortly, stirred vigorously for 3 min, then centrifuged for 10-15 min. Samples (0.05 cm3) were then withdrawn from the chloroform phase in both tubes, they were diluted with acetonitrile to 5 cm³ and the picrate concentration was measured at 380 nm with a UV spectrophotometer. The association constants (K_a) were calculated according to Eq. (1).

Bis (methyl-4,6-0-benzylidene-2,3-dideoxy-a-D-galactopyranosido[2,3-b][3',2'-k])-1,4,7,10,13,16-hexaoxacyclooctadecane and bis (methyl-4,6-O-benzylidene--2,3-dideoxy-a-D-galactopyranosido[2,3-b][2',3'-k])-1,4,7,10,13,16-hexaoxacyclooctadecane (5a and 5b)

Methyl-4,6-O-benzylidene-a-D-galactopyranoside (4) (5.64 g; 20.0 mmol) was dissolved in THF (120 cm³) and 50% KOH solution (6.72 g; 60.0 mmol) was added to it while stirring.; The mixture was stirred at 60 °C for 2 h, then a solution of diethyleneglycol ditosylate (8.28 g; 20.0 mmol) in THF (50 cm³) was added. The reaction mixture was refluxed, with stirring, for 36 h. After cooling, the potassium tosylate precipitate was filtered off and the filtrate was evaporated to dryness in vacuum. The residue was dissolved in chloroform (40 cm³), washed with water $(3 \times 20 \text{ cm}^3)$, dried over Na₂SO₄, and evaporated to dryness in vacuum to obtain the crude product (5.2 g). This was subjected to chromatographic separation on an Al_2O_3 (150 g) column (2.2×40 cm) using benzene - chloroform eluting agent (2:1). The product

(150 g) could (2.2 × 40 cm) using benzete = encodoron charge agent (2.1). The product was crystallized from ethanol. Isomer I (5a or 5b): 0.7 g; 9.9%. M.p. 164–169 °C, $[\alpha]_D^{22} + 164^\circ$ (c = 1.92, chloroform) (*lit.* [3] m.p. 168–170 °C, $[\alpha]_D^{22} + 170.6^\circ$). Isomer II (5a or 5b): 0.3 g; 3.4%. M.p. 250–252 °C, $[\alpha]_D^{22} + 157.7^\circ$ c = 1.88, chloroform (*lit.* [3] m.p. 240 °C, $[\alpha]_D^{22} + 162.9^\circ$.

C₃₆H₄₈O₁₄ (704.8). Calcd. C 61.29; H 6.82. Found C 61.15; H 6.71%. ¹H-NMR (CDCl₃), both isomers: δ 7.2-7.5 (m, 10H, Ar); 5.49 (s, 2H, CH-Ph); 4.90 (d, 2H, J = 2.6 Hz, $C_1 - H$); 4.40-3.50 (m, 28H); 3.40 (s, 6H, CH_3O). MS (200 °C); m/e 704 (1.6%, M^+), 496 (25%), 149 (64%), 121 (23%), 105 (76%), 99 (50%), 73 (100%), 45 (99%).

Bis(methyl-4,6-O-benzylidene-2,3-dideoxy-β-D-galactopyranosido[2,3-b][3',2'-k])--1,4,7,10,13,16-hexaoxacyclooctadecane and bis(methyl-4,6-0-benzylidene-2,3--dideoxy- β -D-galactopyranosido[2,3-b][2',3'-k])-1,4,7,10,13,16-hexaoxacyclooctadecane (7a and 7b)

Starting from methyl-4,6-O-benzylidene-β-D-galactopyranoside (6) (4.5 g; 16.0 mmol), the reaction was effected as given above. After cooling, the reaction mixture was filtered, the precipitate extracted with chloroform $(2 \times 40 \text{ cm}^3)$, the extract was combined with the tetrahydrofuran filtrate and evaporated to dryness in vacuum. The reasidue was rubbed with warm water $(5 \times 50 \text{ cm}^3)$, suspended in cold THF (30 cm^3) and stirred cold for 1 h. The product was filtered off suspended in anhydrous ethanol (40 cm³), stirred for 1 h and filtered off again to obtain 7a and 7b (1.6 g; 28.4%). Recrystallization was effected from a mixture of chloroform and petroleum ether. M.p. 218-244 °C, $[\alpha]_{42}^{22}$ +44.9° (c = 1.52, CHCl₃). C₃₈H₄₈O₁₄ (704.8).Calcd. C 61.29; H 6.82. Found C 61.11; H 6.69%.

¹H-NMR (CDCl₃): δ 7.26-7.70 (m, 10H, Ar); 5.50 (s, 2H, CH-PH); 4.40-3.62 (m, 30H), 3.53 (s, 6H, OCH₃).

MS (200 °C): m/e 704 (5.6% M^+).

Bis(methyl-4,6-O-benzylidene-2,3-dideoxy-α-D-glucopyranosido[2,3-b][3',2'-n])--1,4,7,10,13,16,19,22-octaoxacyclotetracosane and bis(methyl-4,6-O-benzylidene--2,3-dideoxy-α-D-glucopyranosido[2,3-b][2',3'-n])-1,4,7,10,13,16,19,22--octaoxacyclotetracosane (9a and 9b)

Compound 1 (22.6 g; 80.0 mmol) was dissolved in anhydrous THF (300 cm³). Under stirring, 50% aqueous KOH solution (26.8 g; 240.0 mmol) was added to the solution and it was stirred at 60 °C for 1 h. A solution of triethyleneglycol ditosylate (46.0 g; 100.0 mmol) in THF (200 cm³) was then added and the mixture was stirred at the temperature of boiling for 42 h, After cooling, the preciptate was filtered off, extracted with chloroform $(2 \times 100 \text{ cm}^3)$, the extract was combined with the tetrahydrofuran filtrate and evaporated to dryness in vacuum. The residue was rubbed with hot water $(5 \times 50 \text{ cm}^3)$, dissolved in chloroform (250 cm³), dried over Na₂SO₄, filtered and evaporated to dryness in vacuum to obtain the crude product (3.36 g). This was recrystallized twice from anhydrous ethanol to obtain 9a + 9b (8.0 g; **25.3%**), m.p. 120–129 °C, $[\alpha]_{22}^{25}$ +45.6° (c = 1.68, CHCl₃). ¹H-NMR (CDCl₃): δ 7.6–7.2 (m, 10H, Ar); 5.50 (s, 2H, CH–Ph); 4.78 (d, 2H, J = 3.6

Hz, C_1 -H); 4.40-3.35 (n, 42H); 3.42 (s, 6H, OCH₃).

C40H56O16 (792). Calcd. C 60.61; H 7.07. Found C 60.92; H 7.18%.

 $\overset{\text{MS}}{\text{(200 °C):}} \begin{array}{c} m/e & 792 & (1.3\%, M^+), 149 & (37\%), 105 & (50\%), 99 & (32\%), 91 & (36\%), 89 \\ (35\%), 87 & (40\%), 73 & (72\%), 45 & (100\%). \end{array}$

Bis(-2,3-dideoxy-D-glucopyranosyl[2,3-b][3',2'-k])-1,4,7,10,13,16--hexaoxacyclooctadecane (11)

Crown ether 3a (2.0 g; 2.84 mmol) was stirred with 2N hydrochloric acid (40 cm³) for 8 h at 90 °C. After cooling, the reaction mixture was neutralized with saturated $NaHCO_3$ solution and evaporated to dryness in vacuum. The residue was dissolved in anhydrous ethanol (40 cm³), filtered with clarifying carbon and evaporated to dryness; this procedure was repeated with anhydrous ethanol (20 cm³). The product 11 (0.7 g; 49.3%) was recrystallized from a mixture of ethanol and ether; m.p. $65-67 \,^{\circ}$ C, $[\alpha]_{a}^{22} + 20.0 \ (c = 1.6, CH_{3}OH)$ (equilibrium value).

C20H36O15 (500). Calcd. C 48.00; H 7.20. Found C 47.88; H 7.14%.

Bis(methyl-2,3-dideoxy-a-D-glucopyranosido[2,3-b][3,'2'-k])-1,4,7,10,13,16--hexaoxacyclooctadecane (12)

Compound **3a** (3.80 g; 5.40 mmol) was stirred with glacial acetic acid on a boiling water bath for 1 h. Water (40 cm³) was then added in small portions during 5 min and stirring was continued for 10 min. After cooling, the solution was evaporated to dryness in vacuum, water $(2 \times 20 \text{ cm}^3)$ and toluene $(2 \times 30 \text{ cm}^3)$ were added and evaporated to dryness again, to obtain 12 (2.8 g; 98%). Recrystallization was effected from a mixture of ethanol and petroleum ether. M.p. $158 - 160^{\circ}$ C, $[\alpha]_{22}^{22} + 107.3$ (c = 1.72, CH₃OH). ¹H-NMR (D₂O(: δ 4.83 (d, 2H, J = 1.8 Hz, C₁-H), 4.1-3.40 (m, 32H), [3.35

(s, 6H, OCH₃).

C22H40014 (528.5). Calcd. C 50.00; H 7.57. Found C 50.30; H 7.65%.

Bis(methyl-2,3-dideoxy-4,6-di-O-acetyl-α-D-glucopyranosido[2,3-b][3',2'-k])--1,4,7,10,13,16-hexaoxacyclooctadecane (13)

Compound 12 (1.5 g; 2.84 mmol) was treated with a mixture of pyridine (5.6 cm³) and acetic anhydride (5.6 cm³) while cooling. The solution was allowed to stand at room temperature for 24 h then evaporated to dryness in vacuum. Toluene (15 cm³) was added to the residue, evaporated again and the residue was crystallized from methanol to obtain 13 (1.1 g; 55.6%), m.p. 102–104 °C, $[\alpha]_{22}^{22}$ +79.4 (c = 1.44, CHCl₃). ¹H-NMR (CDCl₃): δ 4.81 (d, 2H, J = 2.5 Hz, C₁-H), 4.3–3.5 (m, 28H), 3.40 (s, 6H,

2 OCH₃), 2.08 (s, 12H, 4 COCH₃).

C₃₀H₄₈O₁₈ (696). Calcd. C 51.72; H 6.89. Found C 51.94; H 6.79%.

Bis(methyl-2,3-dideoxy-6-O-tosyl-a-D-glucopyranosido-[2,3-b][3',2'-k])--1,4,7,10,13,16-hexaoxacyclooctadecane (14)

Compound 12 (1.6 g; 2.84 mmol) was dissolved in anhydrous pyridine (7 cm³) and a solution of p-toluenesulfonyl chloride (1.2 g; 6.29 mmol) in anhydrous pyridine (6 cm³) was added. Te mixture was allowed to stand at room temperature for 24 h then evaporated to drynes in vacuum on a water bath of 40 °C temperature. The residual syrup was dissolved in chloroform (18 cm³), washed with saturated solutions of KSHO, KHCO, and with water, dried over Na₅SO₄ and evaporated to dryness in vacuum to obtain 14 (1.45 g; 32.0%). Recrystallization was effected from a mixture of methanol and ether. M.p. 67-70 °C, $[\alpha]_{22}^{22}+52.3$ (c = 1.48,

CHCl₃). ¹H-NMR (CDCl³): δ 7.8–7.2 (m, 8H, Ar), 4.68 (d, 2H, J = 3.5 Hz, C₁–H), 4.24 (d, 4H, J = 2.4 Hz, C₆–H(, 3.9–3.5 (m, 26H), 3.32 (s, 6H, 2 OCH₃), 2.42 (s, 6H, 2 Ph–CH₃). C₃₆H₅₂O₁₈S₂ (836.5). Calcd. C 51.67; H 6.20; S 7.66. Found C 51.45; H 6.21; S 7.54%.

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REACTIONS OF MONO- AND DIARYLIDENECYCLOALKANONES WITH THIOUREA AND AMMONIUM RHODANIDE, VII*

SYNTHESIS OF 2-ALKYLMERCAPTO-4-PHENYLBENZO [*h*]-QUINAZOLINES

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4-phenyl-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)thione (**II**) was synthesized by the base-catalyzed reaction of 2-benzylidene-1-tetralone (**I**) and thiourea. Oxidation of **II** yielded the corresponding quinazolinone (**III**), while alkylation gave the hydrohalides of 2-alkylmercapto-4-phenyl-3,4,5,6-tetrahydrobenzo[h]quinazoline (**IVa**, **b**); these were oxidized in two steps through 2-alkylmercapto-4-phenyl-5,6-dihydrobenzo[h]quinazolines (**VIa**, **b**) into 2-alkylmercapto-4-phenylbenzo[h]quinazolines (**VIIa**, **b**).

Methods suitable for synthesizing benzo[h]quinazolines have recently been surveyed by MUNSLOW and DELIA [2]. These synthetic methods usually start from 1-tetralone using some nitrogen-containing nucleophilic reagent (e.g., acetamide, benzamide, guanidine, urea, etc.). TAYLOR et al. synthesized 8-methoxy-5,6-dihydrobenzo[h]quinazoline-2(1H)-thione from the enamine derivative of 6-methoxy-tetralone and thiourea [3]. MAMAEV and SEDOVA prepared several 4-aryl-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-ones from 1-tetralone, aromatic aldehydes and urea, and the heterocycles of the products were subjected to aromatization by different methods [4]. Some members of this compound family are regarded as agents possessing potential pharmacological activity [5].

In a previous paper we reported that base-catalyzed reactions of some 2-arylidenecyclohexanones and thiourea gave 4-aryl-3,4,5,6,7,8-hexahydro--2(1H)-quinazolinethiones [6]. These were allowed to react with alkyl halides to obtain 2-alkylmercapto-4-phenyl-3,4,5,6,7,8-hexahydroquinazolines [7]; partial aromatization of these compounds yielded 2-alkylmercapto-5,6,7,8-tetrahydroquinazolines. The above reactions have now been examined starting from 2-benzylidene-1-tetralone. Structure verification of the products was based on elemental analysis data and spectroscopic methods (IR, ¹H-NMR, UV).

The IR spectrum of II (Table I) has no longer the $\nu C=O$ band of starting ketone (1660 cm⁻¹), the valence vibration of the NH group appears as

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^{*} For Part VI, see Ref. [1]



a broad band in the range $3000-3300 \text{ cm}^{-1}$, and the thioamide II band can be assigned at 1195 cm⁻¹. The ¹H-NMR spectrum (Table I) excludes the possibility that the ring in the middle has an aromatic structure, since the multiplet between $\delta 1.6-2.9$ ppm can be attributed to the 5-CH₂ and 6-CH₂

puno	15 00	Formula M.w.	UV(ethanol)		IR, cm ⁻¹	¹ H-NMR		
Comp	м.р., °С	Yield, %	$\lambda_{\max},$ nm	log ε	(KBr pellets)	$\delta \operatorname{ppm}(\mathrm{DMSO-}d_6)$		
п	195 (d.)	$\substack{ C_{18}H_{16}N_2S\\ 292.41\\ 91}$	229 267 300	4.32 4.24 3.77	νNH 3000-3300 νC=C 1670 Thioamide II 1195	$\begin{array}{c} 1.6\!-\!2.9 \ \mathrm{m} \ \mathrm{4H} \ \mathrm{CH}_2 \\ 4.95 \ \mathrm{d} \ \mathrm{1H} \ \mathrm{CH}^a \\ 7.0\!-\!7.9 \ \mathrm{m} \ \mathrm{9H} \ \mathrm{Ar} \\ 9.0; \ 9.7 \ \mathrm{s} \ \mathrm{2H} \ \mathrm{NH}^b \end{array}$		
ш	212 (d.)	$\substack{\substack{C_{18}H_{16}N_2O\\276.34\\46}}$	228 269 302	4.29 3.95 3.79	vNH 3000-3300 Amide I 1650	1.3–1.8 m 4H CH ₂ 2.0–2.5 4.7 s 1H CH 6.5–7.2 m 9H Ar°		
IVa	174—178	C ₁₉ H ₁₉ IN ₂ S 434.35 78	257 350	4.87 3.98	$v = NH^+ 2400 - 3300$ vC = C 1675	$\begin{array}{c} 1.5-2.9 \text{ m } 4\text{H } \text{CH}_2 \\ 2.8 \text{ s } 3\text{H } \text{SCH}_3 \\ 5.55 \text{ s } 1\text{H } \text{CH}^4 \\ 7.0-7.8 \text{ m } 9\text{H } \text{Ar} \\ 10.0-11.8 \text{ s } 2\text{H } = \overset{ }{\text{NH}^{+4}} \end{array}$		
IVb	205 - 212	$\substack{ C_{20}H_{21}BrN_2S\\ 401.38\\ 97}$	$\frac{241}{346}$	4.31 3.13	$v = {\rm NH^+} 2400 - 3250$ v C = C 1675	1.2 t 3H CH ₃ 1.8 - 3.0 m 4H CH ₂ 3.0 - 3.9 m 2H SCH ₂ 5.5 d 1H CH ^a 7.0 - 7.9 m 9H Ar		

Table I

Recorded in CD₃COOL

^d Disappeared on the effect of D_2O

^e Recorded in $\text{CDCl}_3 + \text{DMSO-}d_6$

protons. The structure of III is confirmed unambiguously by the IR spectrum (Table I) (ν NH: 3000-3300, Amide I 1650 cm⁻¹).

In the IR spectra of IVa, b, the ionic NH group is indicated by the band between 2400-3300 cm⁻¹. Alkylation at the sulfur atom is confirmed by the signals in the ¹H-NMR spectra assignable to the SCH₃ and SCH₂ groups



($\delta 2.8$ and $\delta 3.0-3.9$ ppm). These chemical shifts are in good agreement with chemical shifts of the corresponding groups in 2-alkylmercaptoquinazolines prepared by us previously [7].

Liberation of the corresponding bases from the salts IVa, b was also attempted. At room temperature compounds Va, b transform, with slight decomposition, into the aromatic compounds VIa, b; this already occurs during purification. When the reaction mixture was made alkaline at 0 °C, Va, b could be isolated; these compounds gradually changed into VIa, b on standing. In the ¹H-NMR spectrum of Va (CDCl₃), the 4-CH can be assigned at δ 4.9 ppm as a triplet with a low coupling constant, which can be attributed to a long-distance coupling with 5-CH₂. The same was observed with the δ 4.95 ppm signal attributed to 4-CH in the spectrum of Vb. In the spectra of Va, b,

the 5-CH₂ and 6-CH₂ are found at $\delta 2.0$ and 2.7 ppm, respectively, while in VIa, b the four protons appear in a narrow interval (see Table II). This change indicates that the phenyl ring is, similarly to the case of the quinazoline derivatives described previously, in axial position [8]. The ready oxidation of Va, b is explained by the fact that in these compounds the phenyl group is in axial position, and as a result of aromatization this ring can assume quasicoplanar position, hence the energetically favoured diphenyl conjugation can develop [9]. In the IR spectra VIa, b, obtained by oxidation from IVa, b (Table II), the vNH band is absent, and the aromatic skeletal vibration characteristic of aromatic pyrimidines [8] can be found at 1525 cm⁻¹. In the ¹H-NMR spectrum (Table II), the signal of 4-CH disappears, the complex SCH₂ multiplet simplifies into a quartet owing to the elimination of the centre of asymmetry; the complex multiplet due to the 5-CH₂, 6-CH₂ groups in IVa, b is now simplified owing to the appearance of a second aromatic ring.

pune		Formula M.w.	UV (ethanol)		IR, cm ⁻¹	¹ H-NMR
Compe	м.р. «С	Yield, %	λ _{max} , logs		(KBr pellets)	ð ppm (CDCl ₃)
VIa	109—113	C ₁₉ H ₁₆ N ₂ S 304.42 53 ^a 82 ^b	229 266 347	4.31 4.43 3.93	<i>v</i> C=C _{Ar} 1525°	$\begin{array}{c} {\rm 2.65~s~3H~SCH_3} \\ {\rm 2.6-3.1~m~4H~CH_2} \\ {\rm 7.0-7.8~m~8H~Ar} \\ {\rm 8.2-8.6~m~1H~Ar} \end{array}$
VIb	72—75	$\begin{array}{c} C_{20}H_{18}N_2S\\ 318.45\\ 69^a\\ 70^b \end{array}$	230 266 347	4.01 4.16 3.65	νC=C _{Ar} 1525°	1.5 t 3H CH_3 2.7 - 3.0 m 4H CH_2 3.25 q 2H $SCH_2 J = 7Hz$ 7.0 - 7.8 m 8H Ar 8.2 - 8.6 m 1H Ar
VIIa	98-105	$\substack{ C_{19}H_{14}N_2S \\ 302.40 \\ 40 }$	238 267 298 311 357 378	4.51 4.55 4.20 4.16 3.62 3.65	νC=C _{Ar} 1530°	2.75 s 3H SCH ₃ 7.0 -7.9 m 10H Ar 8.9 -9.2 m 1H Ar
VIIb	74 (d.)	$\begin{array}{c} C_{20}H_{16}N_{2}S\\ 316.43\\ 20\end{array}$	238 269 298 311 356 377	4.44 4.48 4.12 4.07 3.55 3.59	$\nu C = C_{Ar} 1530^{\circ}$	1.54 t 3H CH ₃ 3.37 q 2H SCH ₂ $J = 7$ Hz 7.2-8.0 m 10 H Ar 8.9-9.3 m 1H Ar

			TT
 a	h	0	
 a			

^a Oxidized with K₃[Fe(CN)₆] ("A") ^b Oxidized with singlet oxygen ("B")

•Very intense multiplet band

The structures of VIIIa, **b** obtained on dehydrogenation were confirmed by the ¹H-NMR and UV spectra. The ¹H-NMR spectra have no 5-CH₂ and 6-CH₂ signals. It should be mentioned here that the signal of 10-H shows a paramagnetic shift in the IVb—VIIb series (Table III). This can be explained

Compound	Chemical shift (8 ppm) 10-H
IVb	$7.6 - 7.9^{a}$
Vb	$7.8 - 8.1^{b}$
VIb	$8.2 - 8.6^{b}$
VIIb	8.9-9.3 ^b

Table III

^a Recorded in $\text{CDCl}_3 + \text{DMSO-}d_6$

^b Recorded in CDCl₃

by the anisotropic effect of the $= N^+H$ group and the ring current in the heteroaromatic ring. The UV spectra of VIIa, b (Table II) greatly differ from the spectra of the starting VIa, b; the formation of a chromophore with a condensed cyclic system results in new maxima.

Experimental

The IR spectra were recorded with a Specord F5, the ¹H-NMR spectra with a Perkin Elmer R12 (60 MHz) spectrometer. UV spectra were obtained with a Perkin Elmer 402 spectro-photometer.

The elemental analysis data were within the limits of experimental error.

The starting material 2-benzylidene-1-tetralone was prepared by aldol condensa tion [10].

The syntheses of 4-phenyl-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-thione (II) and -2(1H)-one (III), of the hydrohalides of 2-alkylmercapto-4-phenyl-3,4,5,6-tetrahydrobenzo-[h]quinazoline (IVa, b), 2-alkylmercapto-4-phenyl-3,4,5,6-tetrahydrobenzo[h]quinazoline (Va, b) and of 2-alkylmercapto-4-phenyl-5,6-dihydrobenzo[h]quinazoline (VIa, b) were effected analogously to the preparation of quinazoline derivatives described by us earlier [6-8]. Other data of II, III and IVa, b are given in Table I.

2-Methylmercapto-4-phenylbenzo[h]quinazoline (VIIa)

Compound VIa (1.0 g; 0.0033 mol) and elemental sulfur (0.21 g; 0.0066 mol) were powdered in a mortar and the mixture was heated on an oil bath at 230 °C for 3 h. After cooling, the brown melt was dissolved in ethanol, and the crystals which separated on cooling were recrystallized from ethanol.

The analogous compound VIIb was obtained in the same way and crystallized from ethanol.

Other data of VIa, b and VIIa, b are given in Table II.

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A MODEL FOR BILAYER ADSORPTION FROM BINARY NONIDEAL LIQUID MIXTURES ON SOLID SURFACES

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The bilayer model of adsorption from binary nonideal liquid mixtures onto solid surfaces is discussed theoretically and examined using experimental excess adsorption data available from literature. A physical explanation of the adsorption parameters appearing in the isotherm equations, and of the existence of azeotropic point is presented. This interpretation is illustrated by a suitable model investigation, which shows the influence of the phase-exchange equilibrium constants and of the bulk phase nonideality parameter on the total excess adsorption isotherm and the excess referring to the list and 2nd adsorbed layers.

Introduction

Many theoretical and experimental papers have been published dealing with adsorption from solutions onto solids. In the majority of them the monolayer adsorption model is assumed [1-3]. On the other hand, it is known that such a model is unrealistic because it is thermodynamically inconsistent [4]. As shown by Tóth [5-6], the conception of the monolayer adsorption is in a contradiction to the structural properties of liquid systems such as association, hydrogen bonds, formation of polar and unpolar structures, etc. These phenomena create a demand for a multilayer adsorption model to be introduced. Moreover, the monolayer adsorption model implies that the surface phase is autonomous; that means, the interactions between bulk and surface phase are neglected. An assumption which is acceptable for ideal systems for which the monolayer adsorption model is a good representation of the true physical situation [7]. The theory of multilayer adsorption from liquid mixtures onto solids, based on a lattice model, has been discussed in few papers only [8-11]. This theoretical approach to liquid adsorption seems to be a most realistic one, but its application to experimental data is difficult because theoretical equations describing adsorption equilibria contain a large number of various parameters. It should, therefore, be interesting to find simple models of multilayer adsorption, which could be easily applied for

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interpretation of experimental data. Some of them have already been proposed [12-13], but they are useful for detecting the existence of a multilayer adsorption rather than for a quantitative description of the multilayer effects.

In many cases the surface phase may well be represented by a bilayer model [4], especially for systems showing small differences in the molecular sizes of the components and a weak energetic heterogeneity of the adsorbent surface. For these reasons we shall propose a simple quantitative description of the bilayer adsorption from binary nonideal bulk solutions assuming meanwhile that the surface phase is ideal. It is the so-called IAP model [14] applied by SCHAY *et al.* [15], DÉKÁNY and NAGY [16], ASH *et al.* [17], when describing the liquid adsorption onto homogeneous solid surfaces. ASH *et al.* [17] have justified precisely the reality of the assumptions underlying this particular model.

In the first part of our consideration, the equations for the excess bilayer adsorption isotherms are derived utilizing the equilibrium constants of the phase-exchange reactions between the molecules of the 1st and the 2nd layer. The next part of our paper explains the formation of the S-shape isotherms which are observed in several cases. Our theoretical equations will be examined taking several experimental data for analysis. The temperature effects in the bilayer adsorption will also be discussed.

Excess adsorption isotherms for bilayer adsorption

Our consideration is based on the following assumptions:

- a) the surface phase is bilayer and ideal,
- b) the total number of moles in the surface phase is constant,
- c) the molecular sizes of both components are equal,
- d) the adsorbent surface is energetically homogeneous.

Further, we assume that the adsorption process may be represented by the following phase-exchange reactions leading to the adsorption equilibrium between the bulk phase (1) and the adsorption region (s),

$$1^{s(2)} + 2^{s(1)} \ge 1^{s(1)} + 2^{(s)^2} \tag{1}$$

$$2^{s(2)} + 1^1 \gtrsim 2^1 + 1^{s(2)} \tag{2}$$

where $1^{s(k)}$ and $2^{s(k)}$ (k = 1, 2) denote the molecules of 1st and 2nd component in the *k*-th adsorbed layer, respectively. Eq. (1) represents the phase-exchange between the 2nd and 1st adsorbed layer, whereas Eq. (2) represents the similar exchange between the bulk phase and 2nd adsorption layer.

Let us introduce the following notation: $n_i^{s(k)}$, for i, k = 1, 2, is the number of the moles of the *i*-th component in the *k*-th adsorbed layer; $n^s = n_1^{s(k)} + n_2^{s(k)}$ is the total number of moles of both components in the 1st or 2nd adsorbed layer; $x_i^{s(k)}$ is equal to $n_i^{s(k)}/n^s$; x_i^s and x_i^1 are the mole fractions of the *i*-th component in the bilayer and bulk phase, respectively. Then,

$$x_1^{s(k)} + x_2^{s(k)} = 1$$
 for $k = 1, 2$ (3)

$$x_1^{\mathrm{s}} + x_2^{\mathrm{s}} = 1$$
 (4)

$$x_1^1 + x_2^1 = 1$$
 (5)

where,

$$x_1^{\rm s} = (n_1^{\rm s(1)} + n_1^{\rm s(2)})/2n_1^{\rm s} = 0.5[x_1^{\rm s(1)} + x_1^{\rm s(2)}]^{\rm s}$$
(6)

Let the symbols K_1 and K_2 denote the equilibrium constants for phase-exchange reactions (1) and (2), respectively. Then we have,

$$K_1 = \frac{x_1^{s(1)} x_2^{s(2)}}{x_2^{s(2)} x_2^{s(1)}} \tag{7}$$

$$K_2 = \frac{x_1^{\rm s(2)} a_2^{\rm l}}{x_2^{\rm s(2)} a_1^{\rm l}} \tag{8}$$

where $a_i^1 = x_i^1 \cdot f_i^1$ is the activity of the *i*-th component in the bulk phase, f_i^1 is the suitably defined activity coefficient.

The equilibrium constants K_1 and K_2 are connected with the adsorption energies in the following way,

$$K_1 = \exp\left[(\varepsilon_1^{(1)} - \varepsilon_2^{(1)})/RT\right]$$
(7')

and

$$K_2 = \exp\left[(\varepsilon_1^{(2)} - \varepsilon_2^{(2)})/RT\right]$$
(8')

In Eqs (7'), (8') the quantity $\varepsilon_l^{(k)}$ is the increase in potential energy per mole of the *i*-th component, which is connected with the transition of molecules from the (k + 1)-th layer to the *k*-th layer. This definition for $\varepsilon_l^{(k)}$ corresponds with that introduced by SCHAY [19] and used by DÉKÁNY and NAGY [16].

Combining Eqs (6), (7) and (8) we obtain,

$$x_{1}^{s} = \frac{0.5 K_{12} a_{12}^{1}}{1 + K_{12} a_{12}^{1}} + \frac{0.5 K_{2} a_{12}^{1}}{1 + K_{2} a_{12}^{1}}$$
(9)

$$a_{12}^1 = a_1^1 / a_2^1 \tag{10}$$

and,

$$K_{12} = K_1 \cdot K_2 = \exp\left[(\varepsilon_1 - \varepsilon_2)/RT\right] \tag{11}$$

or,

$$K_{12} = \frac{x_1^{\mathrm{s}(1)} \cdot x_2^1}{x_2^{\mathrm{s}(2)} \cdot x_1^1} \tag{11'}$$

The adsorption energy ε_i is defined to be the sum $(\varepsilon_i^{(1)} + \varepsilon_i^{(2)})$.

Above, the equilibrium constant K_{12} is related to the following phase-exchange reaction,

$$1^{1} + 2^{\mathfrak{s}(1)} \gtrsim 1^{\mathfrak{s}(1)} + 2^{1} \tag{12}$$

which describes the equilibrium between the 1st adsorbed layer and the bulk phase.

The total adsorption excess of the 1st component may be expressed as follows,

$$n_{1}^{\sigma} = 2n^{s}(x_{1}^{s} - x_{1}^{1}) = n^{s}(x_{1}^{s(1)} - x_{1}^{1}) + n^{s}(x_{1}^{s(2)} - x_{1}^{1}) = n_{1}^{\sigma(1)} + n_{1}^{\sigma(2)}$$
(13)

where, n_1^{σ} is the simple sum of the adsorption excesses for the 1st and the 2nd adsorbed layer. It follows from Eqs (9) and (13) that for IAP model, the excesses $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ are given by

$$n_{1}^{\sigma(1)} = \frac{n^{s}[K_{12}a_{12}^{1} - x_{1}^{1}(K_{12}a_{12}^{1} + 1)]}{1 + K_{12}a_{12}^{1}}$$
(14)

and

$$n_1^{\sigma(2)} = \frac{n^{\rm s}[K_2 a_{12}^1 - x_1^1(K_2 a_{12}^1 + 1)]}{1 + K_2 a_{12}^1} \tag{15}$$

Thus, the total adsorption excess, n_1^{σ} , is given by the following equation,

$$n_{1}^{\sigma} = \frac{n^{s} x_{1}^{1} [(2K_{12} \cdot K_{2} f_{12}^{1} - K_{12} - K_{22} a_{21}^{1} + (K_{12} + K_{2}) f_{12}^{1} - 2]}{1 + K_{12} \cdot K_{2} (a_{12}^{1})^{2} + (K_{12} + K_{2}) a_{12}^{1}}$$
(16)

where $f_{12}^1 = f_1^1 / f_2^1$.

Similarly, for the IBP model (ideal behavior of both adsorbed and bulk phases), we obtain,

$$n_1^{\sigma} = \frac{n^s x_1^1 [(2K_{12} \cdot K_2 - K_{12} - K_2) x_{12}^1 + K_{12} + K_2 - 2]}{1 + K_{12} \cdot K_2 (x_{12}^1)^2 + (K_{12} + K_2) x_{12}^1}$$
(17)

Let us assume now, that the bulk solution is regular. Then, for such a model of the bulk phase, the variable f_{12}^1 may be expressed as follows,

$$f_{12}^1 = \exp\left[\hat{q}(1-2x_1^1)\right] \tag{18}$$

where $\hat{q} = q/RT$.

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The quantity q is the temperature independent constant characterizing molecular interactions in the bulk regular solution. It follows from the theory of regular solutions that q is a measure of the deviation of a given solution from Raoult's law. In the case of completely miscible components \hat{q} can assume values from minus infinity (strong negative deviations from ideality) to 2.0 (strong positive deviations from ideality), *i.e.*, $\hat{q} \in /-\infty$, +2. Combining Eq. (18) with Eqs (14) and (15) we obtain the equations for $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ which correspond to the model with a regular equilibrium bulk phase.

Accepting the relationships (16) and (18) we will consider four following cases,

1.
$$K_{12} > K_2 > \exp\left[\hat{q}(2x_1^1 - 1)\right]$$
 for IAP model (19)
and

$$K_{12} > K_2 > 1$$
 for IBP model (20)

Eqs. (19) and (20) are equivalent to the following inequalities,

$$n_1^{\sigma(1)} > n_1^{\sigma(2)} > 0 \tag{21}$$

and

$$1 > x_1^{\mathsf{s}(1)} > x_1^{\mathsf{s}(2)} > x_1^{\mathsf{l}} > 0 \tag{22}$$

2.
$$0 < K_{12} < K_2 < [\exp \hat{q}(2x_1^1 - 1)]$$
 for IAP model (23)

and

$$0 < K_{12} < K_2 < 1 \qquad \qquad \text{for IBP model} \tag{24}$$

Whence

$$n_1^{\sigma(1)} < n_1^{\sigma(2)} < 0 \tag{25}$$

and

$$0 < x_1^{\rm s(1)} < x_1^{\rm s(2)} < x_1^{\rm 1} < 1 \tag{26}$$

3.
$$K_{12} > \exp \left[\hat{q} (2x_1^1 - 1) \right]$$
 for IAP model (27)

$$K_2 = \exp \left[\hat{q} (2x_1^1 - 1)
ight]$$
 then $n_1^\sigma > 0$ (28)

and

$$K_{12} > 1$$
 for IBP model (29)

$$K_2 = 1 \qquad \qquad \text{then } n_1^\sigma > 0 \qquad \qquad (30)$$

Appropriate relations are true then $n_1^{\sigma} < 0$.

In this case we obtain,

$$n_1^{\sigma} = n^{\sigma(1)} \text{ and } n_1^{\sigma(2)} = 0, \text{ i.e., } x_1^{s(2)} = x_1^1$$
 (31)

and adsorption is exactly a monolayer one.

4.
$$K_{12} = K_2 = K \neq \exp \left[\hat{q}(2x_1^1 - 1)\right]$$
 for IAP model (32)

and

$$K_{12} = K_2 = K \neq 1$$
 for IBP model (33)

Whence $n_1^{\sigma} \neq 0$, and Eq. (16) gives,

$$n_1^{\sigma} = \frac{2n^{\rm s}[Ka_{12}^1 - x_1^1(Ka_{12}^1 + 1)]}{1 + Ka_{12}^1} \quad \text{for IAP model}$$
(34)

and

$$n_{1}^{\sigma} = \frac{|2n^{s} x_{1}^{1}(K-1)|}{1+K x_{12}^{1}} \qquad \text{for IBP model} \qquad (35)$$

Moreover,

$$x_1^{s(1)} = x_1^{s(2)}$$

i.e., the mole fraction of the 1st component in the bilayer region is constant. It means that the surface phase consists of more than two adsorption layers.

The S-shape isotherms in bilayer adsorption

The S-shape isotherms, *i.e.*, isotherms type IV and V in terms of the SCHAY-NAGY isotherm classification [3], can be explained on the basis of a bilayer adsorption.

It is known, that these isotherms contain the azeotropic point: $x_{1, az.}^1 \in (0, 1)$. At this point,

$$n_1^{\sigma(1)}(K_{12}, x_{1, az.}^1) + n_1^{\sigma(2)}(K_2, x_{1, az.}^1) = 0$$
 (36)

Inserting Eqs (14) and (15) into Eq. (36) we get the following relationship between K_{12} and K_{2} ,

$$K_{12} = f_{21}^{1}(x_{1, az.}^{1}) + \frac{f_{21}^{1}(x_{1, az.}^{1}) - K_{2}}{1 - 2x_{1, az.}^{1}[1 - K_{2}f_{12}^{1}(x_{1, az.}^{1})]} \quad \text{for IAP model} \quad (37)$$

and

$$K_{12} = 1 + \frac{1 - K_2}{1 - 2x_{1, az.}^1(1 - K_2)}$$
 for IBP model (38)

Above

$$f_{21}^1 = (f_{12}^{1!}) - 1 \tag{39}$$

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The variable f_{12}^1 for regular bulk phase is expressed by Eq. (18). First we shall consider Eq. (38). This equation leads to the following inequality,

$$0 < \left(x_{1, \text{ az.}}^{1} = \frac{2 - K_{12} - K_{2}}{2(1 - K_{12}) \cdot (1 - K_{2})} \right) < 1$$
(40)

For a given value of K_2 , the surface azeotrope is observed only in limited range of K_{12} , defined by the following inequalities,

$$K_{12} \ge 2 - K_2,$$
 for $0 < K_2 \le 0.5$ (41)

$$2 - K_2 < K_{12} < \frac{K_2}{2K_2 - 1}$$
, for $0.5 < K_2 < 1$ (42)

for which

$$n_1^{\sigma(1)} > 0, \ n_1^{\sigma(2)} < 0, \ x_1^{\mathfrak{s}(1)} > x_1^{\mathfrak{l}} > x_1^{\mathfrak{s}(2)}, \ \ x_1^{\mathfrak{l}} \in (0, 1)$$
 (43)

and

$$2 - K_2 < K_{12} < rac{K_2}{2K_2 - 1}$$
, for $1 < K_2 < 2$ (44)

$$0 < K_{12} \le rac{K_2}{2K_2 - 1}$$
, for $K_2 \ge 2$ (45)

for which

$$n_1^{\sigma(1)} < 0, \ n_1^{\sigma(2)} > 0, \ x_1^{\mathfrak{s}(1)} < x_1^{\mathfrak{s}} < x_1^{\mathfrak{s}(2)}, \ \ x_1^{\mathfrak{l}} \in (0, 1).$$
 (46)

When $x_{1, az.}^1 = 0.5$, we have

 $K_{12} = (K_2)^{-1}$

It has been explained by TÓTH [5-6], that the inequalities (43) and (46) indicate opposite signs of the adsorption excesses in the 1st and 2nd layers. But, this statement and the relationships (43) and (46) are true for the IBP model only. When the bulk phase is regular or nonideal in general, then Eqs (14) and (15) may rewritten in an alternative way,

$$n_1^{\sigma(1)} = \frac{n^s x_1^1 [K'_{12} - 1]}{1 + K'_{12} x_{12}^1} \tag{14'}$$

where

$$K_{12}'(x_1^1) = K_{12} \cdot f_{12}^1 = K_{12} \exp\left[\hat{q}(1-2x_1^1)
ight]$$
 (14")

and

$$n_1^{\sigma(2)} = \frac{n^{\mathrm{s}} x_1^{\mathrm{l}} [K_2' - 1]}{1 + K_2' x_{12}^{\mathrm{l}}}$$
(15')

where

$$K'_2(x_1^1) = K_2 \exp\left[\hat{q}(1-2x_1^1)\right].$$
 (15")

The variables K'_{12} and K'_{2} are functions of the mole fraction x_1^1 . Taking into account Eqs (14''), (15'') when $x_1^1 \to 0$, $x_1^1 \to 1$, and Eq. (37), we can state that for a given value of K_2 the surface azeotrope is observed in a limited range of K_{12} only. This range is defined by,

$$K_{12} \ge 2e^{-q} - K_2$$
, for $0 < K_2 \le e^{q/2}$ (47)

and

$$2e^{-q} - K_2 < K_{12} < \frac{K_2}{2K_2e^{-q} - 1}$$
, for $K_2 > e^{q/2}$ (48)

$$K_{12} \ge 2e^{-q} - K_2$$
, for $0 < K_2 \le e^{q/2}$ (47')

$$2e^{-q} - K_2 < K_{12} < \frac{K_2!}{2K_2e^{-q} - 1}$$
, for $e^q/2 < K_2 \le e^{-q} - \sqrt{e^{-2q} - 1}$ (49)

$$\frac{K_2}{2K_2 e^{-q} - 1} < K_{12} < 2e^{-q} - K_2,$$

for $e^{-q} - \sqrt{e^{-2q} - 1} < K_2 < e^{-q} + \sqrt{e^{-2q} - 1}$ (50)

$$2e^{-q} - K_2 < K_{12} < \frac{K_2}{2K_2e^{-q} - 1}, \text{ for } e^{-q} + \sqrt{e^{-2q} - 1} \le K_2 < 2e^{-q} \quad [(51)$$

$$0 < K_{12} \le \frac{K_2}{2K_2 e^{-q} - 1}$$
, for $K_2 \ge 2e^{-q}$ (52)

In the case of regular bulk phase, the relationships (43) and (46) are not true in the whole interval: $x_1^1 \in (0, 1)$. It means that the in 1st and 2nd adsorbed layers the surface azeotropes can appear separately, but it does not mean that they will cause the appearance of two azeotropic points on the experimental excess isotherms, being the sum of the excess in the first and the second layers. Taking into account the above considerations we can conclude that the experimentally observed S-shape isotherms may be caused by bilayer adsorption and nonideality of the bulk solution.

Results and Discussion

First, we shall discuss the simplest case of the IBP model. For this model the numerical calculations were carried out on the basis of Eqs (14), (15) and (17). The parameter n^{s} , *i.e.*, the total number of moles in the 1st or 2nd adsorbed layer, was assumed to be unity. The results of the model calculations are shown in Fig. 1.

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In the parts A, B, and C of this Figure the excess adsorption isotherms $n_1^{\sigma(2)}$ (the dotted lines), $n_1^{\sigma(1)}$ (the stronly dashed lines) and $n_1^{\sigma} = n_1^{\sigma(1)} + n_1^{\sigma(2)}$ (the solid lines) are presented for different values of K_{12} and K_2 . Moreover, in the parts A', B' and C', of Fig. 1 the individual isotherms corresponding to the excess isotherms are presented. The labelling is as in the case of the excess isotherms, however, the dotted-dashed line refers to the equal mole fractions in both phases.



Fig. 1. The adsorption isotherms $n_1^{\alpha}(A, B, C)$ and $x_1^{s}(A', B', C')$ calculated according to Eqs (14), (15) and (17) (IBP model) for $K_{12} = 3.125$, $K_2 = 1.25$ (A, A'), $K_{12} = 6.25$, $K_2 = 0.625$ (B, B') and $K_{12} = 2.5$, $K_2 = 0.5$ (C, C'). The solid, dashed and dotted lines denote n_1^{α} and $x_1^{s}, n_1^{\alpha(1)}$ and $x_1^{s(1)}, n_1^{\alpha(2)}$ and $x_1^{s(2)}$, respectively, whereas, the dotted-dashed lines denote $x_1^{s} = x_1^{s}$

In parts A and A' the excess and individual isotherms are presented for $K_{12} = 3.125$ and $K_2 = 1.25$. It can be seen that the isotherms $n_1^{\sigma(1)}$, $n_1^{\sigma(2)}$ and n_1^{σ} are greater than zero in the whole concentration region and $n_1^{\sigma} > n_1^{\sigma(1)} > n_1^{\sigma(2)}$. Moreover, the mole fractions satisfy the following inequality: $x_1^s > x_1^{s(1)} > x_1^{s(2)} > x_1^1$. This result is in good agreement with our earlier discussion and means a gradual change of concentration of the 1st component between the first adsorbed phase and the bulk phase.

The parts B and B' of Fig. 1, show the excess and individual isotherms for $K_{12} = 6.25$ and $K_2 = 0.625$. It can be seen that in this case $n_1^{\sigma(1)} > 0$, $(x_1^{s(1)} > x_1^1)$, but $n_1^{\sigma(2)} < 0$, $(x_1^{s(2)} < x_1^1)$ for $x_1^1 \in (0, 1)$. The isotherm $x_1^s = 0.5$

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 $(x_1^{\mathfrak{s}(1)} + x_1^{\mathfrak{s}(2)}) > x_1^1$ and $n_1^{\sigma} = n_1^{\sigma(1)} + n_1^{\sigma(2)} > 0$ for $x_1^1 \in (0, 1)$, but the latter is essentially of type III according to the classification by SCHAY and NAGY [3]. It represents a transition to S-shape isotherm shown in the parts C, C' of Fig. 1, In this figure $K_{12} = 2.5$, $K_2 = 0.5$, so $n_1^{\sigma(1)} > 0$, $(x_1^{\mathfrak{s}(1)} > x_1^1)$, but $n_1^{\sigma(2)} < 0$, $(x_1^{\mathfrak{s}(2)} < x_1^1)$ for $x_1^1 \in (0, 1)$. Moreover, $x_1^{\mathfrak{s}} > x_1^1$, $(n_1^{\sigma} > 0)$ for $x_1^1 \in (0, x_{1, az.}^1 > and <math>x_1^{\mathfrak{s}} < x_1^1$, $(n_1^{\sigma} < 0)$ for $x_1^1 \in < x_{1, az.}^1$ 1).

On the basis of Eq. (40) we obtain $x_{1, az.}^1 = 0.67$. In this case, an adsorption azeotrope is formed because inequalities (41) are fulfilled, *i.e.*, $K_2 = 0.5$ and $K_{12} = 2.5 > 2 - K_2 = 1.5$. Moreover, in the part A of Fig. 1, the isotherms n_1^q , $n_1^{q(1)}$, $n_1^{q(2)}$ are shown, which have been calculated for $K_{12} = 1.56$ and $K_2 = 0.625$. The isotherm n_1^q is S-shaped with the azeotropic point $x_{1, az.}^1 = 0.44$ [see Eq. (40)]. For this isotherm inequalities of type (41) are fulfilled, *i.e.*, $0.5 < K_2 = 0.625 < 1$, and $(2 - K_2 = 1.38) < K_{12} = 1.56 < \{K_2/(2K_2 - 1) = 2.5\}$. It should be pointed out that the inequality (41) is not fulfilled for the constants K_{12} and K_2 , which corresponds to the parts B and B' of Fig. 1. For this reason the S-shape isotherms are not here observed.

Our model calculation presented in Fig. 1 is confirmed by appropriate results obtained from our analysis of three experimental systems taken from the literature (see Table I): ethylene dichloride (1)-benzene(2) on titania gel (Fig. 2A), ethylene dichloride (1)-benzene(2) on charcoal (Fig. 2B) and benzene (1)-ethylene dichloride (2) on activated carbon (Fig. 2C). The labelling is as in Fig. 1. Since the liquid mixtures are ideal, Eqs (9) and (13) with $f_{12}^1 = 1$ were used for calculating the parameters K_{12} , K_2 , n^s and the standard deviation (SD). These parameters are summarized in Table I. It can be seen from this Table and Fig. 2A, that for the system ethylene dichloride (1)-benzene (2) on titania gel the constant $K_2 = 1$ and $n_1^{\sigma(2)} = 0$. According to our earlier discussion it means that the adsorption is purely monolayer, i.e., $n_1^{\sigma} = n_1^{\sigma(1)}$ and $x_1^{s(2)} = x_1^1$. The experimental excess adsorption isotherm for the system ethylene dichloride(1)-benzene (2) on charcoal is an S-shaped one. The parameters $K_{12} = 4.83$ and $K_2 = 0.08$ fulfil the relationship (41). The azeotropic point calculated according to Eq. (40) is equal to 0.41, but from the experimental data it is 0.40. According to our considerations presented in section 2 for IBP model, from Fig. 2B we can conclude that $n_1^{\sigma(1)} > 0$, $n_1^{\sigma(2)} < 0$ and $x_1^{s(1)} > x_1^1 > x_1^{s(2)}$ for $x_1^1 \in (0, 1)$. From physical point of view the observed S-shape isotherm can be explained as follows. The liquid mixture is nearly ideal but the contact with the solid creates some interactions between the slightly apolar surface of the charcoal and molecules of ethylene dichloride. In addition there will appear the interactions between π -electrons of the molecules, which are mainly in the second adsorbed layer. It should be pointed out that for this system the S-shaped form of the adsorption isotherm is not caused by the heterogeneity of the solid surface [20-21]. In Fig. 2C the results are shown of our numerical analysis for the system: benzene (1)-ethylene

dichloride (2) on activated carbon. They seem to be in good agreement with the model investigation presented in Fig. 1B. This excess isotherm is not Sshaped because the inequality (42) is not fulfilled. Moreover, benzene is adsorbed preferentially in the whole concentration region, *i.e.*, $n_1^{\sigma(1)} > 0$ and $n_1^{\sigma(1)} >$ $> n_1^{\sigma} > n_1^{\sigma(2)}$, but $n_1^{\sigma(2)} < 0$ for $x_1^1 \in (0, 1)$. Following COLTHARP and HACKER-MAN [22], this preferential adsorption of benzene on activated carbon is induced by similarity between the basal faces of the surface and benzene,



Fig. 2. The experimental excesses n_1^{σ} (circles) for adsorption of ethylene dichloride(1)-benzene(2) on titania gel(A), benzene(1)-ethylene dichloride(2) on activated carbon(B), ethylene dichloride-(2)-benzene(1) on charcoal (C) in comparison to the theoretical excesses (the solid lines) calculated from Eqs (9) and (13). The dashed and dotted lines denote $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$, respectively

despite of the difference in hexagon sizes. Moreover, for the systems illustrated in Fig. 1, the minimum number of layers which are necessary for the thermodynamic consistency of the surface phase, t, is equal to unity (t = 1) on the basis of the well known EVERETT's formula [4]. The cross sectional areas which are necessary for calculating the parameter t, were taken from reference [23]. The individual isotherms, corresponding to those shown in Fig. 2, may be easily calculated by using the suitable parameters n^{s} , K_{12} and K_{2} from Table I.

In Fig. 3, the model investigation is presented for IAP model. Taking into account all the model studies done here some conclusions can be drawn concerning the influence of bilayer adsorption and non-ideality of the bulk phase on the total excess isotherm, n_1^{σ} . Part A of Fig. 3 shows the total adsorp-

No. of ad. system	Liquid mixture	Adsorbent	Temp. °C	n ^s [mmole/g]	K.,	K_2	SD	Ref. to adsorption system	Ref. to activity coefficients
1.	ethylene dichloride(1)-benzene(2)	titania gel	20	2.070	1.25	1.00	0.006	[27]	$f_1^1 = f_2^1 = 1$
2.	ethylene dichloride(1)-benzene(2)	charcoal	20	0.983	4.83	0.08	0.001	[26]	$f_1^1 = f_2^1 = 1$
3.	benzene(1)-ethylene dichloride(2)	activated carbon	30	1.027	18.85	0.74	0.005	[28]	$f_1^1 = f_2^1 = 1$
4.	benzene(1)-cyclohexane(2)	graphit	20	0.481	1.93	1.53	0.001	[26]	[26]
5	benzene(1)-cyclohexane(2)	charcoal	20	1.650	11.63	1.73	0.030	[26]	[26]
6.	benzene(1)-cyclohexane(2)	silica gel	0	1.820	12.91	4.84	0.020	[25]	[29]
7.	benzene(1)-cyclohexane(2)	silica gel	30	1.720	9.42	4.32	0.014	[25]	[29]
8.	benzene(1)cyclohexane(2)	silica gel	60	1.621	6.88	3.71	0.011	[25]	[29]
9.	benzene(1)-cyclohexane(2)	graphit	30	0.151	2.51	2.51	0.001	[30]	[29]
10.	benzene(1)-cyclohexane(2)	spheron	20	0.270	3.65	3.65	0.001	[26]	[26]
11.	benzene(1)-ethyl alcohol(2)	graphit	25	0.191	6.96	6.96	0.092	[31]	[32]
12.	benzene(1)-ethyl alcohol(2)	graphit	20	0.180	15.87	15.87	0.070	[31]	[32]
13.	n-hexane(1)-benzene(2)	silica gel	35	0.291	3.95	1.01	0.007	[33]	[34]
14.	butyloamine(1)-benzene(2)	charcoal	20	1.521	29.55	1.05	0.010	[26]	[26]
15.	n-hexane(1)-benzene(2)	tin oxide gel	35	0.240	4.97	1.76	0.002	[33]	[32]
16.	ethyl alcohol(1)-benzene(2)	Bi oxide+Mo oxide	45	0.390	16.07	1.97	0.007	[34]	[35]
17.	ethyl alcohol(1)-benzene(2)	boehmite	20	1.472	33.37	2.79	0.001	[36]	[32]
18.	benzene(1)-n-heptane(2)	silica gel	25	1.650	29.36	1.57	0.004	[37]	[38]

Table I

Parameters calculated according to the bilayer adsorption model for different experimental systems

tion excess n_1^{σ} vs. x_1^1 calculated for $K_{12} = 3.125$, $K_2 = 0.625$ and different values of \hat{q} running the values: +2, +1, 0, -1, -2 (the curves a, b, c, d, e, respectively). Parts B and C of this Figure show the excess isotherms $n_1^{\sigma(1)}$ (part B) and $n_1^{\sigma(2)}$ (part C), and they correspond to the curves n_1^{σ} (see part A). It appears from Fig. 3 that for a regular bulk phase showing positive deviation from Raoult's rule, the S-hape excess isotherms $n_1^{\sigma(1)}$, $n_1^{\sigma(2)}$, n_1^{σ} are predicted (curves a, b). For this particular case of IAP model, the S-shaped excess



Fig. 3. The theoretical excesses n_1^{σ} (A), $n_1^{\sigma(1)}$ (B) and $n_1^{\sigma(2)}$ (C) calculated for $K_{12} = 3.125$, $K_s = 0.625$ and regular bulk phase q = 2(a), 1(b), 0(c), -1(d) and -2(e). The dashed lines are calculated for $K_{12} = 6.25$, $K_2 = 1.25$ and q = -1

isotherms are obtained for the 1st and the 2nd adsorbed layer, in contrast to the isotherms $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ for IBP model, which are still U-shaped (positive or negative in the whole interval of x_1^1).

Besides, the existence of the total S-shape isotherm n_1^{σ} is in agreement with the inequality (47).

The curves c in Fig. 3 present the situation when the parameter $\hat{q} = 0$ (ideal bulk solution). The total isotherm n_1^{σ} is U-shaped and component 1 is preferred obviously through the total concentration range. Simultaneously, the isotherms $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ are U-shaped too, but they have opposite signs, *i.e.*, $n_1^{\sigma(1)} > 0$, and $n_1^{\sigma(2)} < 0$ for $x_1^1 \in (0, 1)$. For $\hat{q} = -1$ (curve d), and $\hat{q} = -2$ (curve e) the total isotherms as well as the excess isotherms $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ are S-shaped also. But, the values n_1^{σ} , $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ are negative for $x_1^1 \in (0, x_{1, az}^1)$ and positive for higher concentrations. Such adsorption systems

are known in literature, e.g., chloroform (1)-acetone (2) on charcoal [3]. The existence of the total S-shape isotherm, n_1^{σ} (curves a, b, d, e) is in agreement with the inequalities (47) (q > 0) and (47') (q < 0). It is interesting to note that for $K_{12} = 6.25$, $K_2 = 1.25$ and $\hat{q} = -1$ (the dashed line f in Fig. 3) the total excess isotherm is not S-shaped, in contrast to that one calculated for $K_{12} = 3.125$, $K_2 = 0.625$, $\hat{q} = -1$ (the solid line d in Fig. 3). It finds support in the inequality (47).



Fig. 4. The experimental excesses n_1^{σ} (circles) for adsorption of benzene(1)-cyclohexane(2) on graphite at 20 °C (A) and benzene(1)-cyclohexane(2) on charcoal (B) in comparison to the theoretical one's (the solid lines). The dashed and dotted lines denote $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$, respectively

Summing up the results obtained, we can draw the following conclusions: the change of sign of the excess adsorption isotherms may be caused by nonideality of the bulk phase and as well as by overlapping effects of adsorption in 1st and in 2nd layer. Figure 4 shows the experimental adsorption data (circles) with comparison to the theoretical isotherms for two systems taken from the literature: benzene (1) - cyclohexane(2) on graphite at 20 °C (part A), and benzene (1) - cyclohexane (2) on charcoal (part B) (for detailed informations see also Table I). In this case the bulk solution is a regular one, and the parameter $\hat{q} = 0.543$ [17]. The total isotherm for the system on graphite is slightly S-shaped and $n_1^{\sigma(1)} > 0$ for $x_1^1 \in (0, 1)$, but the isotherm $n_1^{\sigma(2)}$ is S-shaped too. This behaviour of the excess isotherm may be probably caused by nonideality of the bulk phase (see the model studies presented in Fig. 3). Moreover, it is in agreement with the inequality (47).

In part B of Fig. 4, the excess isotherms are shown for the same liquid mixture but different adsorbent charcoal.

Let us consider an interesting case of the adsorption investigated in various temperatures. For this purpose the analysis of the system: benzene(1) – cyclohexane (2) on silica gel at 0 °C, 30 °C and 60 °C was carried out. This system was investigated experimentally by SIRCAR *et al.* [25]. The detailed results of numerical analysis for this system are reported in Table 1. Figure 5 (part C) shows the experimental excess adsorption data (0 °C-circles, 30 °C -triangles, 60 °C -squares) compared with the theoretical isotherms calculated



Fig. 5. The experimental excesses $n_1^{\sigma}(C)$ for adsorption of benzene(1)-cyclohexane(2) on silica gel at 0 °C (1), 30 °C (2) and 60 °C (3) in comparison to the theoretical one's. The theoretical excesses $n^{\sigma(1)}$ and $n_1^{\sigma(2)}$ are showed in the parts A and B of this Figure, respectively

Jor the parameters from Table I. In parts B and A of this Figure the excess isotherms $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$ for various temperatures (curve 1-0 °C, curve 2-30 °C, curve 3-60 °C) are shown. For the purpose of the illustration of the temperature dependence of the isotherms n_1^{σ} , $n_1^{\sigma(1)}$ and $n_1^{\sigma(2)}$, the dependence of ln K_1 , ln K_2 and ln K_{12} upon (1/T) is shown in Fig. 6. These relationships for systems investigated are linear. Differences of the adsorption potentials [see Eqs (7'), (8') and (11)] can be evaluated from the slopes of these straight lines,

$$\frac{\partial \ln K_1}{\partial \left(\frac{1}{T}\right)} = R^{-1} \left[\varepsilon_1^{(1)} - \varepsilon_2^{(1)} \right] = 0.55$$
(53)

$$\frac{\partial \ln K_2}{\partial \left(\frac{1}{T}\right)} = R^{-1} \left[\varepsilon_1^{(2)} - \varepsilon_2^{(2)} \right] = 0.41$$
(54)

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$$\frac{\partial \ln K_{12}}{\partial \left(\frac{1}{T}\right)} = R^{-1}[\varepsilon_1 - \varepsilon_2] = 0.96$$
(55)

The above results are in a good agreement with the relationship: $\ln K_{12} =$ $= \ln K_1 + \ln K_2$.

From Eqs (53-55) and Fig. 6, the following conclusion can be drawn: the variation of adsorption with temperature is bigger in the 1st adsorbed



Fig. 6. Linear dependences of $\ln K_1$ (1), $\ln K_2$ (2) and $\ln K_{12}$ (3) upon 1/T for adsorption of benzene (1)-cyclohexane(2) on silica gel

layer than in the 2nd one, and simultaneously the influence of the temperature on phase-exchange reaction between the 1st and the 2nd layer is bigger than on this reaction between the 2nd adsorbed layer and the bulk solution.

It appears from Table I that the variation of the parameters K_{12}, K_2 and n^s with temperature is regular.

Besides, this system and other systems available from the literature were investigated using the IAP adsorption model. The related numerical results are reported in Table I. In this Table the essential information about the investigated systems is also given. We would like to stress that for the four systems from Table I, the parameters $K_{12} = K_2$. It means that the surface phase consists of more than two layers. Therefore, these systems were tested by applying EVERETT's equation (see, e.g., the paper [17]) and the parameter t was estimated also. For systems: benzene(1)-cyclohexane(2) on graphite at 30 °C and benzene(1)-cyclohexane(2) on spheron, t = 2,

whereas, for systems: benzene (1)-ethyl alcohol (2) on graphite at 20 °C and at 25 °C, t = 3. For the latter systems the bilayer model is not quite adequate. but it seems to be more useful for an analysis of the experimental data than the well-known EVERETT's isotherm equation.

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SCHIFF BASE COMPLEXES OF Zn(II), Cd(II) AND Hg(II) DERIVED FROM BENZIDINE AND ACETYLACETONE

(SHORT COMMUNICATION)

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Though the schiff base complexes derived from salicylaldehyde and [mines have been studied widely [1-3], the references to schiff base complexes aerived from acetylacetone and benzidine (ACB) have not been much noticed d4, 5]. Therefore, a study of these complexes has been undertaken.

The procedure for the preparation of complexes and physical measurements used in this investigation were the same as already described elsewhere [6]. The results of analysis are shown in Table I.

The complexes are intense yellow to pale yellow, stable against light and atmosphere, soluble in polar solvents and insoluble in common organic solvents.

The conductivity values in DMF are in the range of 20-40 Ohm cm² mol⁻¹ at 10^{-3} M concentration, indicating a non-electrolyte nature.

In its electronic spectrum the schiff base (ACB) has two bands at 240 nm and 355 nm. The intense band at 355 nm in the ligand is replaced by a more complicated broad band of varying intensity, when they are coordinated to metal ions, which is taken as an evidence for complex formation. These bands are attributed to $\pi \to \pi^*$ transitions [7].

The selected IR frequencies for ACB and it complexes with their tentative assignments are listed in Table I. An earlier study [8] on the schiff bases of this type concluded that they exist in the phenolamine form. The strong band in the $1630-1600 \text{ cm}^{-1}$ region is attributed to the C=N stretching mode. The other authors [9, 10] have reported this band in the range of $1550-1600 \text{ cm}^{-1}$ for α,β -unsaturated ketone Schiff bases. In the complexes, this band is shifted to the lower frequency region (Table I), indicating that the coordinate bond is formed between the N of the azomethine group and metal ion [11, 12]. The lower values reported here are probably due to coupling with the 1600 cm⁻¹ band of phenyl nucleus. There are three bands in the region between $1600-1560 \text{ cm}^{-1}$ in the ligand and complexes. They are tentatively

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Complex	Decomp. temp. or M.P. (°C)	M(%)	N(%)	Cl(%)	${ m Ligand}_{ m (ACB)}$	${ m Zn}({ m ACB}) { m Cl}_2$	Cd(ACB) Cl ₂	${ m Hg(ACB)} { m Cl}_2$	Assignment
Ligand (ACB)	172	-	7.92 (8.04)	-	1625	1605	1610	1602	$\nu C=N$ stretching
					1605	1568	1560	1550	$\nu C = C + \nu C - C$ stretching
$Zn(ACB)Cl_2$	230	$13.28 \\ (13.49)$	5.68 (5.78)	$13.99 \\ (14.65)$	1555	1535	1525	1526	
$Cd(ACB)Cl_2$	298	20.97 (21.10)	5.18 (5.27)	13.78 (13.37)	$\begin{array}{c}1515\\1485\end{array}$	1500	1505	1498	
$Hg(ACB)Cl_2$	201	33.08 (32.37)	4.68 (4.52)	12.01 (11.46)	1450	1445	1450	1440	
		(· · · /	1326	1329	1330	1322	Coupled $\nu C - O$
					1290	1286	1292	1288	Phenolic vC-O stretching
					-	532	525	520	B
						516	505	502	vM-N stretching

Analytical and IR spectral data for schiff base complexes of Zn(II), Cd(II) and Hg(II)

assigned to coupled vC=C and vC-C stretching modes. These bands show some remarkable changes in their frequencies on going from the ligand to metal complexes. The strong band at 1290 cm⁻¹ in ligand ACB due to phenolic (CO) stretching vibration is retained in the complexes without much alteration. These observations emphasize that the ligand has not undergone deprotonation while reacting with metal(II) chlorides [13]. Analytical data also support this view. Taking into consideration the observations of other authors [4, 5, 12] on M-N stretching assignment, the medium intensity bands appearing in the 500-530 cm⁻¹ region for these metal complexes are assigned to M-N stretching vibration.

On going from the spectrum of free ligand to those of the complexes in freshly prepared DMSO- d_6 solution in NMR, we observe chemical shifts towards lower fields. This is due to electron withdrawal by the metals from nitrogen atoms and the remarkable deshielding effect, supporting the hypothesis that the complexes studied are N-bonded. On coordination, the methyl and azomethine protons are shielded in M(II) complexes. This phenomenon is generally observed in NMR of the first and second row transition elements [14]. It is further observed that the methyl and azomethine protons appear as doublets in the complexes. This can be readily explained as these protons in tetrahedral symmetry will be considered dissymmetric [15].

The ACB ligand is more flexible than *bis*(salicylidene)benzidine, hence complex may exist in monomeric form, but the models for it are more strained

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than in the dimeric form (see structures). A definite conclusion in this case is not possible because of the insolubility of complexes in common organic solvents. In view of these observations, we propose the following dimeric structure for the complexes in which metal ions have the same coordination numbers.

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BENZOYL HYDRAZONE DERIVATIVES OF MONO(CYCLOPENTADIENYL)-TITANIUM(IV) CHLORIDE

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The reactions of mono(cyclopentadienyl)titanium(IV) chloride $(CpTiCl_3)$ with monobasic benzoyl hydrazones (BHyH) (molar ratios 1:1 and 1:2) and dibasic benzoyl hydrazones $(BHy'H_2)$ (molar ratio 1:1) have been carried out in refluxing dichloromethane. These reactions lead to the formation of the products of the type: $CpTiCl_2(BHy)$, $CpTiCl(BHy)_2$ and CpTiCl(BHy'). The compounds thus obtained have been characterized on the basis of elemental analysis, electrical conductance measurements and spectral (IR, NMR and electronic) data.

Introduction

There are quite a few examples in the literature of schiff bases derived from monoacylhydrazines [1-7]. Acetone acylhydrazones, RCONHN=CMe₂ (R = Me, Et or Ph), have been reported to behave as bidentate ligands coordinating to metal ions in the keto form and in the deprotonated enol form, vielding six-coordinated complexes of Co(II), Ni(II) and Cu(II) [2]. Schiff bases derived by the condensation of benzoyl hydrazine with benzoylacetone or dibenzovlmethane form Ni(II) complexes in which ligands show tridentate nature [4]. A series of Cu(II) complexes of salicylaldehyde-acylhydrazones have also been reported [7]. However, there is hardly any example of hydrazone complex containing mono(cyclopentadienyl)titanium(IV) moiety. These hydrazones have been of further interest as they are widely used in the treatment of several diseases such as tuberculosis, leprosy and mental disorder [8]. Thus, in view of the versatile chelating ability and biological activity of hydrazones, it has been considered of interest to study the reactions of mono- and dibasic benzovl hydrazones with CpTiCl₃. The structure of the hydrazones used for the present studies are depicted below:

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(CyPBHyH)

where $R = C_4H_3O$, R' = H(FBHyH) $R = C_6H_5$, R' = H(BBHyH) $R = (p \cdot OCH_3)C_6H_4$, R' = H(ABHyH) $R = C_6H_5$, $R' = CH_3(AcPhBHyH)$ $R = C_6H_5$, $R' = C_6H_5(BzPhBHyH)$



(CyHxBHyH)



Experimental

Dichloromethane (BDH) was dried by refluxing it over phosphorus pentoxide and then finally distilled over anhydrous calcium chloride. $CpTiCl_3$ was prepared by the method reported earlier [9]. Hydrazones were synthesized by the condensation of benzoyl hydrazine with aldehyde/ketone in the presence of ethanol [10].

All operations were carried out under strict anhydrous conditions and glass apparatus with standard interchangeable joints was used throughout the work.

Titanium was determined gravimetrically as TiO₂, chlorine as AgCl and nitrogen by KJELDAHL's method.

Physical measurements

The infrared spectra of the complexes were recorded on a Perkin-Elmer 621 Spectrophotometer in KBr pellets. Electrical conductance measurements were made on Elico conductivity Bridge type CM 82T. The electronic and nuclear magnetic resonance spectra of the complexes were recorded on Perkin-Elmer 4000A and Perkin-Elmer R32 spectrophotometers, respectively.

Reaction of mono(cyclopentadienyl)titanium(IV)chloride^{*} with benzoyl hydrazone (mole ratio 1:1 or 1:2)

To the calculated amounts of CpTiCl_3 and benzoyl hydrazone dichloromethane ($\sim 60 \text{ mL}$) was added. The reaction mixture was refluxed till the evolution of HCl gas ceased. After the completion of the reaction, the solvent was removed under reduced pressure and the solid compound so obtained was recrystallized from the mixture of *n*-hexane and dichloromethane.

For the sake of brevity, the details of the reactions of ${\rm CpTiCl}_3$ with different benzoyl hydrazones are summarized in Table I.

Results and Discussion

The reactions of mono(cyclopentadienyl)titanium(IV) chloride with monobasic benzoyl hydrazones in mole ratios 1:1 and 1:2 in refluxing dichloromethane lead to the formation of the complexes of the type: CpTiCl₂ (BHy) and CpTiCl(BHy)₂, respectively. The reactions are the following:

$$\begin{array}{l} \text{CpTiCl}_{3} + \text{BHyH} \xrightarrow{\text{CH}_{3}\text{Cl}_{3}} \text{CpTiCl}_{2}(\text{BHy}) + \text{HCl} \uparrow \\ \\ \text{CpTiCl}_{3} + 2 \text{ BHyH} \xrightarrow{\text{CH}_{2}\text{Cl}_{3}} \text{CpTiCl}(\text{BHy})_{2} + 2 \text{ HCl} \uparrow \end{array}$$

where [BHy]⁻ represents the anion of the corresponding monobasic benzoyl hydrazone, BHyH.

These complexes are red to brown solids and are soluble in common organic solvents such as dimethylformamide, dichloromethane, tetrahydrofuran, benzene, acetone and chloroform. They are susceptible to hydrolysis and the electrical conductance measurements in dimethylformamide indicate that they are non-electrolytes.

Mono(cyclopentadienyl)titatnium(IV) chloride reacts with dibasic benzoyl hydrazones (mole ratio 1:1) in refluxing dichloromethane to yield the products of the type: CpTiCl(BHy').

$$CpTiCl_3 + BHy'H_2 \xrightarrow{CH_2Cl_2} CpTiCl(BHy') + 2 HCl^{\uparrow}$$

where $[BHy']^{2-}$ is the anion of the corresponding dibasic benzoyl hydrazone, $BHy'H_2$.

The complexes are red solids and are also soluble in common organic solvents. They show non-electrolytic behaviour in dimethylformamide.

The elemental analyses and physical data of the reaction products are given in Table I.

Infrared spectra

Infrared spectra of benzoyl hydrazones show medium to strong bands in the regions 3260-3150 and 1625-1580 cm⁻¹ which are considered to be due to v(NH) or v(NH) mixed with hydrogen bonded v(OH), and v(C=N)

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Reactants (molar ratio)	Reflux- ing	Product and colour	Found (calcd) %				
	time (hours)		Ti	C1	N		
1	2	3	4	5	6		
$CpTiCl_3 + FBHyH (1:1)$	35	CpTiCl ₂ (FBHy) Red	12.11 (12.06)	17.00 (17.85)	6.13 (7.05)		
$CpTiCl_3 + FBHyH (1:2)$	40	$\begin{array}{c} { m CpTiCl(FBHy)_2} \\ { m Red} \end{array}$	8.18 (8.33)	6.20 (6.17)	8.92 (9.75)		
$CpTiCl_3 + BBHyH (1:1)$	35	CpTiCl ₂ (BBHy) Orange	11.33 (11.76)	17.11 (17.41)	6.01 (6.88)		
$CpTiCl_3 + BBHyH (1:2)$	35	CpTiCl(BBHy) ₂ Orange	7.40 (8.05)	5.94 (5.96)	8.83 (9.42)		
$CpTiCl_3 + ABHyH (1:1)$	30	CpTiCl ₂ (ABHy) Red	10.64 (10.96)	15.23 (16.22)	5.59 (6.40)		
$CpTiCl_3 + ABHyH (1:2)$	35	CpTiCl(ABHy) ₂ Orange-red	7.25 (7.31)	5.63 (5.41)	7.65 (8.55)		
$CpTiCl_3 + AcPhBHyH (1:1)$	35	CpTiCl ₂ (AcPhBHy) Brown	12.02 (11.37)	17.37 (16.83)	5.80 (6.65)		
$CpTiCl_3 + AcPhBHyH (1:2)$	40	CpTiCl(AcPhBHy) ₂ Dark brown	7.89 (7.69)	6.52 (5.69)	8.35 (8.99)		
$CpTiCl_3 + BzPhBHyH (1:1)$	35	CpTiCl ₂ (BzPhBHy) Orange	10.56 (9.91)	14.98 (14.67)	5.05 (5.79)		
$CpTiCl_3 + BzPhBHyH (1:2)$	40	CpTiCl(BzPhBHy) ₂ Yellow-orange	7.50 (6.41)	5.19 (4.74)	7.02 (7.50)		
$CpTiCl_3 + CyPBHyH (1:1)$	40	CpTiCl ₂ (CyPBHy) Brown	12.45 (12.44)	17.80 (18.41)	6.52 (7.27)		
$CpTiCl_3 + CyPBHyH (1:2)$	40	CpTiCl(CyPBHy) ₂ Brown	8.99 (8.69)	6.94 (6.43)	10.19 (10.17)		
$CpTiCl_3 + CyHxBHyH (1:1)$	40	CpTiCl ₂ (CyHxBHy) Brown	10.84 (11.99)	17.31 (17.76)	6.72 (7.02)		
$CpTiCl_3 + CyHxBHyH (1:2)$	45	$CpTiCl(CyHxBHy)_2$ Dark-brown	9.19 (8.27)	7.00 (6.12)	8.95 (9.68)		
$CpToCl_3 + SBHy'H_2 (1:1)$	35	CpTiCl(SBHy') Red	12.79 (12.39)	9.01 (9.17)	6.62 (7.24)		
$CpTiCl_3 + VBHy'H_2 (1:1)$	35	CpTiCl(VBHy') Brown-red	10.86 (11.49)	7.67 (8.51)	6.06 (6.72)		
$CpTiCl_3 + AcPh'BHy'H_2 (1:1)$	35	CpTiCl(AcPh'BHy') Red-orange	11.93 (11.95)	9.36 (8.85)	5.99 (6.99)		

Reactions of CpTiCl₃ with benzoyl hydrazones

(azomethine) vibrations, respectively [5]. In the spectra of complexes the first band is absent, while there is a decrease of $\sim 35-10 \text{ cm}^{-1}$ in the latter band thus indicating the complete deprotonation of hydrazones in the complexes
Table II

Comp ex	$rac{ u(\mathrm{NH})+}{ u(\mathrm{OH})}$	v(C=0)	$\nu(C=N)$	ν(C—O)	v(C—H) sym	ν(C—C) asym	ð(С—Н) і.р.	ð(C—H) o.p.
CpTiCl ₂ (FBHy)	_	_	1630w ⁴ 1605s ^b	-	3030m	1440m	1015m	820m
CpTiCl(FBHy) ₂	-	-	1635w 1610s	-	3040m	1440m	1015m	825m
CpTiCl ₂ (BBHy)	-	-	1630m 1610m	-	3040m	1440m	1015w	810s
CpTiCl(BBHy) ₂	-	-	1630m 1600m	-	3040m	1440m	1010m	810s
CpTiCl ₂ (ABHy)	-	-	1630m 1585s	-	3035m	1440m	1020s	810s
CpTiCl(ABHy) ₂	-	-	1635w 1585s	-	3030w	1440m	1020m	820m
CpTiCl ₂ (AcPhBHy)	-	-	1640m 1575s	-	3035m	1445m	1020s	800s
CpTiCl(AcPhBHy) ₂	-	-	1640m 1575s	-	3035m	1445s	1020s	800s
CpTiCl ₂ (BzPhBHy)	-	-	1630w 1595s	-	3030m	1450s	1020m	800m
$CpTiCl(BzPhBHy)_2$	-	-	1630m 1600s	-	3040m	1445s	1020m	810m
CpTiCl ₂ (CyPBHy)	-	-	1620w 1590w	-	3040m	1440m	1020m	810m
CpTiCl(CyPBHy) ₂	-	-	1625m 1590m	-	3035 m	1440m	1020m	800s
CpTiCl ₂ (CyHxBHy)	-	-	1625m 1570w	-	3035m	1440m	1020m	800s
CpTiCl(CyHxBHy) ₂	-	-	1620m 1545m	-	3040m	1445m	1020m	800s
CpTiCl(SBHy')	_	_	1630w 1600s	1340s	3035m	1445m	1025m	820s
CpTiCl(VBHy')	-	-	1635w 1575s	1320s	3040m	1445m	1020s	810s
CpTiCl(AcPh'BHy')	_	-	1630w 1590s	1350s	3035m	1440m	1015m	810s

Important infrared frequencies (cm^{-1}) of benzoyl hydrazone derivatives of mono(cyclopentadienyl)titanium(IV) chloride

^a Uncoordinated >C=N vibration ^b Coordinated >C=N vibration

and the coordination of azomethine-nitrogen to the titanium atom [11]. The strong bands between $1670-1645 \text{ cm}^{-1}$ due to amide-I (vC=O) vibration along with bands due to amide-II and -III (ν CN + δ NH) vibrations [12,13] (observed in the region 1540-1510 and 1290-1220 cm⁻¹, respectively) of the ligands are found to be absent in the complexes thus suggesting that these hydrazones are coordinating in the enol form through deprotonation. However, a new weak to medium band in the range 1640-1620 cm⁻¹ can not be assigned to coordinated >C=0 group, but is due to an uncoordinated >C=N- group [14] which seems to have its origin in the $>C=N-N=C \leq 0$ group. The enolization of the ligands in the complexes is confirmed by the appearance of a new strong band in the region 1530-1505 cm⁻¹ due to ν (NCO) vibration [15].

The band appeared in the region $1280 - 1250 \text{ cm}^{-1}$ in the dibasic hydrazones is attributed to the phenolic v(C-O) vibration. In the complexes, this band is found in the region $1350 - 1320 \text{ cm}^{-1}$, suggesting again that the hydroxy group has entered into the bond formation with the titanium moiety [16, 17].

The v(M-N) and v(M-O) vibrations generally absorb in the 600-450 cm⁻¹ region [18-20]. Therefore, the bands observed in the 620-445 cm⁻¹ region in present complexes can tentatively be assigned to v(Ti-O) and v(Ti-N) vibrations, however, it is difficult to make specific assignments. The v(Ti-Ci) vibration occurs in the region 420-390 cm⁻¹ [21].

The presence of π -cyclopentadienyl group in these hydrazone derivatives is indicated by the appearance of bands at *ca.* 3035 cm⁻¹ (symmetric C-H stretching), *ca.* 1440 cm⁻¹ (asymmetric C-C stretching), *ca.* 1020 cm⁻¹ (C-H in-plane deformation) and *ca.* 810 cm⁻¹ (C-H out of plane deformation) in their infrared spectra [22].

The important infrared frequencies of the complexes are given in Table II.

Proton magnetic resonance spectra

The presence of cyclopentadienyl group in complexes is further confirmed by the proton magnetic resonance spectra, recorded in deuterated chloroform, which show a new sharp peak in the range δ 6.8–6.2 ppm corresponding to five protons.

Electronic spectra

The electronic spectra of the complexes, recorded in dimethylformamide, show a single band in the range 24,400-24,350 cm⁻¹ which can be assigned to a charge-transfer transition. The absence of d-d transition rules out the presence of any unpaired electron in the complexes.

Thus, on the basis of elemental analysis, electrical conductance measurements and spectral data, the following structures can be proposed to the complexes, $(Cp)TiCl_2(BHy)$ (A), $(Cp)TiCl(BHy)_2(B)$ and (Cp)TiCl(BHy')(C):



represents the anion of the bidentate monobasic benzoyl hydrazone, where



(C)

represents the anion of the tridentate dibasic benzoyl hydrazone.

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RELATIONSHIP BETWEEN CERTAIN SPECIFIC PROPERTIES AND THE MOLECULAR MASS OF ASYMMETRIC OLIGOMERIC POLYMER-HOMOLOGOUS COMPOUNDS⁺⁺

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Based on literature data a linear relationship has been found between the optical rotation and the reciprocal molecular mass for polymer-homologous oligomeric compounds containing asymmetric carbon atoms (repeating units: L-methionine, α-L-glutamic acid, asymmetric C atom in side-chains: menthyl vinyl ether, methyl propyl vinyl ether). This relationship may be considered as a special form of the equation derived earlier by us. From this it follows that the compounds studied do not form secondary structures under the given experimental conditions. Thus the molecular optical rotation increments of the repeating units have been given. Similar linear relationship has been found between the reciprocal melting point of *α*-L-glutamic acid oligomers, resp. the specific ellipticity of L-Ca-galacturonate oligomers and their reciprocal molecular masses. For the limiting value of the melting point of the homologous series of poly-a-glutamic acid a value of 253.2 °C has been obtained. From the investigation of specific ellipticity it could be established that all the relationships are valid for the equation and for its constants that had already been established earlier for equations of similar type. From the change of the specific ellipticity as a function of the molecular mass, the conclusion can be drawn that no structural change occurs under the given experimental conditions, in agreement with BYSTRICKY et al.

Introduction

Optically active polymers form a relatively new and interesting field of polymer chemistry. Therefore researchers show more and more interest to these polymers. This interest is promoted by the intensive research work carried out on the secondary structures occurring in the solutions of protein and nucleic acids, as well as by the successful advance of stereospecific polymerizations, which can be conveniently studied by means of optical rotation. Part of these works is of preparative, another part is of theoretical character.

From results obtained so far -e.g. from the studies of monotonous polypeptides - the conclusions can be drawn that if the polypeptide is present in form of random coil in a certain solvent (this is the case of solvents capable

⁺ Synthetic linear polymers, XXXVII.: Acta Polym., **32**, 701 (1981); Kolor. Ért., **23**, (1981)

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to destroy H bonds), the optical rotatory dispersion can be already described by the so-called simple or one-term equation of DRUDE [1]:

$$[\alpha]_{\lambda} = \frac{A_0}{\lambda^2 - \lambda_0^2} \tag{1}$$

where λ is the wavelength,

 $[\alpha]_{\lambda}$ is the specific rotation belonging to wavelength λ ,

 A_0 is the rotational constant and

 λ_0 is the so-called dispersion constant.

In order to determine the numerical value of the constants Eq. (1) must be linearized according to YANG and DOTY [2]:

$$[\alpha]_{\lambda} \ \lambda^2 = A_0 + \lambda_0^2 [\alpha]_{\lambda} \tag{2}$$

By plotting $[\alpha]_{\lambda}\lambda^2$ against $[\alpha]_{\lambda}$, a straight line is obtained, the intercept of which is A_0 , and its slope is λ_0^2 .

In general polypeptides are present in a given solvent in helical form. In this case the secondary structure can be described by the empirical equation of MOFFIT and YANG [3]:

$$[\mathbf{M}]_{\lambda}^{0} = \frac{3}{n^{2} + 2} \frac{M_{0}}{100} [\alpha]_{\lambda} = \frac{a_{0}\lambda^{2}}{\lambda^{2} - \lambda_{0}^{2}} + \frac{b_{0}\lambda_{0}^{4}}{(\lambda^{2} - \lambda_{0}^{2})^{2}}$$
(3)

where

 $[\mathbf{M}]^0_{\lambda}$ is the molecular rotation of the polypeptide in vacuum at a wavelength of λ ,

n is the refractive index of the solvent,

 M_0 is the molecular mass of the repeating unit,

 a_0, b_0 and λ_0 are constants, of which a_0 depends on the repeating units, while b_0 and λ_0 on the nature of the helices present, b_0 is the extent of the helix content, which can be determined from the slope of the straight line obtained — on using experimental values — when plotting $[M]^{\lambda}_{\lambda}(\lambda^2 - \lambda_0^2)$ against $1/(\lambda^2 - \lambda_0^2)$. Knowledge of b_0 enables to determine the helix content as a function of the experimental conditions (solvent, pH value, temperature, etc.) [4, 5]. Such types of studies were made by GOODMAN et al. for oligopeptides [6-9].

They established that in the case of $\text{oligo-}\gamma\text{-methyl-L-glutamate}$ in dichloro acetic acid (DCLA) and dimethylformamide (DMF) as solvents helix formation occurs already from the heptamers, while for $\text{oligo-}\beta\text{-methyl-L-}$ -aspartate in chloroform helix formation appears first at the undecamer only. In this latter case the oligomers are present in DMF and DCLA as random coils.

A similarly important characteristic is the contribution of the individual repeating units to the final optical rotation in different solvents. The determination of this quantity is rather difficult by the methods available at present. A possibility is to calculate the molecular rotation from the measured specific rotation data, and to plot it against the molecular mass. From the slope of the straight line thus obtained, the contribution of the molecular rotation of the given repeating unit can be determined. Another method is — according to FREUDENBERG *et al.* [10, 11] — to plot $[M]_{\lambda}/p$ against (p-1)/p for the polymer homologous series of carbohydrates, and to extrapolate $[M]_{\lambda}$ to $p = \infty$ (*i.e.* p - 1/p = 1). From this value the molecular $[M]_{\lambda}$ and the specific rotation $[\alpha]_{\lambda}$ of the repeating unit can be determined (p is the degree of polymerization).

It has been shown earlier [12] that between the specific rotation of oligosaccharides and their molecular mass the following relationship exists:

$$[\alpha]^t_{\lambda} = \frac{a}{M} + b \tag{4}$$

where $[\alpha]_{\lambda}^{t}$ is the specific rotation belonging to the wavelength λ , M is the molecular mass, a and b are constants, of which a is characteristic of the end groups and b of the repeating units.

It has been also shown [13-16] that the value of b of Eq. (4) given in the form as follows:

$$b = \frac{\Phi_k}{M_k} \tag{5}$$

where Φ_k is the molar property of the repeating unit and M_k is its molecular mass, can be used for the calculation of the molar bonding or atomic increments of atoms building up the repeating unit.

On this basis we have given the numerical values for some increments [14-17] not yet published in the literature. Furthermore it has been shown earlier that for the detection of the secondary structure of dissolved macromolecules both the so-called specific mean-square dipole moment $[\bar{\mu}^2/M]$ [18-21], and the specific rotation $[\alpha]$ [12, 20, 22] can be conveniently used. We have established that in the most general case a linear relationship exists between the value of $\bar{\mu}^2/M$ or $[\alpha]$ and the reciprocal molecular mass. The intercept of the straight line thus obtained — which is characteristic of the repeating units — is different if the orientation and rotation of the otherwise identical repeating units differ as e.g. in the case of linear and cyclic poly-(dimethylsiloxane)s [19], linear maltodextrines and cyclic SCHARDINGER dextrines [12], poly(ethylene oxide)s and p-alkylphenol poly(ethylene oxide)s [23].

We have pointed out that the phenomenon has to appear in similar cases so far not yet investigated.

Finally using the data of GOODMAN *et al.* [6-9] we have shown that deviations from the linearity [20-23] indicates the existence of secondary structure. Our results are in complete accordance with those of GOODMAN *et al.* obtained previously by means of other methods.

In spite of the relative rapidity of the method, it can be considered as a deficiency that it supplies no informations at all on the nature of the secondary structure.

Recent investigations

As on the basis of the studies carried out so far no statement of general validity could be established for the rather limited number of experimental data, therefore in the present work further data were applied resp., used concerning the behaviour of macromolecules in solution on the basis of optical rotatory measurements.

The present investigations and calculations were carried out on monotonous oligomer homologous series shown in Table I. In the course of our investigations the specific optical rotation of various oligomers based on

N	Pit	E-d-		Salaant	Range of	Def	Con of H	stants Eq. (4)	rks
10.	Repeating unit	End g	groups	Solvent	tion degree	Kel.	а	ь	Rem ⁸
1	-L-Met-	BOC-	-OMe	HFIP-OH	2-7	[24]	1.69	-70.2	
2	-α-L-Glu-	TFA*	$-\mathbf{H}$	H_2O	2 - 20	[25]	4.97 0.02	$\begin{array}{r}-92.0\\0.0019\end{array}$	**
3	-menthyl vinyl ether-	-	_	Toluene	M _n : 5500- 23,000	[26]	-0.45	-209.7	***
4	-(S)-1-methyl propyl vinyl ether-	_	_	Benzene	M _n : 5200— 7700	[26]	-4.43	214.3	***
5	-Sodium-L- galactu- ronate-	H-	-0H	H_2O	1-64	[27]	-0.23	14.8	
6	-Calcium-L- -galactu- ronate-	H-	-OH	H_2O	1-5	[27]	0.18	14.3	

Table J

Oligomers studied

* Personal communication of the authors

** Constants for Eq. (7)

*** End groups are not given

literature data was plotted against the reciprocal molecular mass, similarly to our method applied earlier. Our results are shown in Figs 1-3.

The reciprocal melting point of $oligo-\alpha-L$ -glutamic acid with trifluoroacetate end group was also plotted as a function of the reciprocal molecular mass (Fig. 4).



Fig. 1. Change of optical rotation of oligo-L-methionines containing tert-butoxy-carbonyl and methoxy end groups as a function of the reciprocal molecular mass in hexafluoro-i-propanol at $25 \,^{\circ}\text{C}$



Fig. 2. Change of optical rotation of oligo-α-L-glutamic acids containing hydrogen and trifluoroacetate end groups as a function of the reciprocal molecular mass in aqueous solution

Finally the specific ellipticity (ϑ) of Ca resp. Na oligogalacturonates in aqueous solution were plotted as a function of the reciprocal masses on the basis of the molecular ellipticity data (Θ) of BYSTRICKY *et al.* [27] (Figs 6 and 7).

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Fig. 3. Change of optical rotation of poly(menthyl vinyl ether)s (MVE) in toluene, and of poly [(S)-1-methyl propyl vinyl ether]s (MPVE) in benzene as a function of the reciprocal molecular mass



Fig. 4. Change of reciprocal melting point of oligo-α-L-glutamic acids containing hydrogen and trifluoroacetate end groups as a function of the reciprocal molecular mass

Discussion

Figures 1-3 show that the plotted points lie with good approximation on a straight line. Consequently relationship (4) — established earlier — which is essentially a special form of the equation

$$\varphi = \frac{a}{M} + b \tag{6}$$

where φ is a specific quantity [12, 16] — is valid also in the case investigated. At the same time the slope (a) and the intercept (b) of the straight lines calculated by the method of averages are also given in the Figures.

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While investigations so far were carried out by us only with oligomeric compounds containing the asymmetric carbon atoms in the main chain, in the recent investigations the asymmetric C atoms of the polymenthyl- and polymethyl-propyl vinyl ethers are situated in the side-chain. The investigations show that this change does not influence the final results. From the results the conclusion can be drawn that no change occurs in the structure of the oligomers investigated in the range of molecular mass under the given experimental conditions. The calculated molecular optical rotation increments of the repeating unit of these oligomers are given is Table II.

In previous papers [12, 16, 28] it was already shown that the reciprocal melting point can also be considered as a specific quantity, and its plotting as a function of the reciprocal molecular mass can be described with a relationship similar to [6]. From Fig. 4 it can be seen that the equation

$$\frac{1}{T_{\rm mp}} = \frac{a}{M} + a \tag{7}$$

is valid also for the melting point $(T_{\rm mp})$ of oligo- α -L-glutamic acid with tri-fluoroacetate end group.

Obviously, from the plotting of Eq. (7) the expected limiting value of the melting point of the poly- α -L-glutamic acid polymer homologous series can be easily determined. The value of this is 253.2 °C on the basis of the intercept of the straight line in Fig. 4.

On the basis of such plotting the determination of the limiting value of the optical rotation is similarly easy and comfortable, in contrats to the com-

Table II

Molecular rotation increments of the repeating units of the oligomers studied $([M_0]_D = [\alpha]_{M_{\infty}} M_0/100, \text{ see: [11]})$

		Molecular mass of the repeating unit: M ₀	Solvent	$[\mathbf{M}_0]_D$
1.	BOC-(L-Met) _n -OMe	131.2	HFIP-OH	- 92.1
2.	Oligo-α-L-glutamic acid trifluoroacetate	129.0	H_2O	-118.7 $24.5 imes 10^{-2*}$
3.	Poly-(menthyl vinyl ether) (MVE)	182.0	Toluene	-381.6
4.	Poly-[(S)-1-methyl propyl vinyl ether]	100.0	Benzene	214.3
5.	Oligo-sodium-L-galacturonate	212.0	H_2O	31.4**
6.	Oligo-calcium-L-galacturonate	209.0	H_2O	29.9**

* Molecular reciprocal melting point increment of the repeating unit

** Molecular ellipticity increment of the repeating unit

plicated methods applied by FREUDENBERG and other authors, as it was pointed out earlier [12] by us.

As the molecular ellipticity is also supposed to be an additive quantity — though it has not been studied yet in detail — therefore we investigated the validity of the additivity in the case of the molecular ellipticity (Θ) of oligo-L-Ca-galacturonate by using the data of BYSTRICKY, KOHN and STICZAY [27]. As can be seen in Fig. 5 the molecular ellipticity of this compound changes



Fig. 5. Change of molecular ellipticity of oligo-L-Ca-galacturonates as a function of the molecular mass

linearly with the molecular mass, therefore, in this case the principle of the additivity can be applied. Therefore we plotted the specific ellipticity as a function of the reciprocal molecular mass. For the time investigations concerning the specific elasticity as a function of the molecular mass are still missing in the literature. From Figs 6 and 7 it can be seen that the points obtained in this manner lie with good approximation on a straight line. Consequently the following relationship — which can be considered as a special form of Eq. (6) — is valid:

$$\vartheta = \frac{a}{M} + b \tag{8}$$

where ϑ is the specific ellipticity,

M is the molecular mass,

a and b are constants, the latter of which is characteristic of the repeating unit.

From the Figures it can be seen that due to the near identical repeating units of the two oligomer homologous series, the values of b are — as expected — nearly the same. Investigations on specific ellipticity showed that all the relations established earlier for Eq. (6) are also valid for Eq. (8) and its constants, resp., as well. The result obtained shows that in the range of mole-

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Fig. 6. Change of the specific ellipticity of poly-L-Na-galacturonates as a function of reciprocal molecular mass in aqueous solution



Fig. 7. Change of the specific ellipticity of oligo-L-Ca-galacturonates as a function of the reciprocal molecular mass in aqueous solution

cular mass investigated no change occurs in the structure of the dissolved macromolecules studied (salts of poly-L-galacturonic acid) upon increasing the molecular mass, and they are present in form of random coils.

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EQUILIBRIUM GEOMETRIES OF URACIL AND SOME OF ITS DERIVATIVES BY THE CNDO/2 METHOD

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The equilibrium geometries for isolated molecules of uracil, thymine (5-methyluracil) and five other methylated uracils, (1-methyl, 3-methyl, 6-methyl, 1,3-dimethyl and 5,6-dimethyl) as well as two different aza-uracils (5-aza and 6-aza) were calculated by PULAY's force method [1] taking advantage of NALEWAJSKI's algorithm [2]. The parameters are compared to X-ray diffraction data in crystals and to each other within this series of compounds.

Introduction

Pyrimidine bases are constituents of nucleic acids and play an important role in basic biological processes. Their reactions are often modelled in solid state [3] and hence several papers deal with their crystal structure [4, 5].

On the other hand, little attention has been paid to the geometries of isolated molecules though the knowledge of these geometries is necessary for studying some theoretical aspects of important phenomena such as photodimerization [6] or for calculating the theoretical vibrational spectra in the gas phase [7].

Some calculations of geometries in the gas phase have already been reported [8, 9]. However, these results at MINDO/2 level [9] are rather doubtful, as the enol tautomer has been reported to be energetically more stable in contradiction to the experiment showing exclusively the stability of the keto tautomer [10].

In the present paper, calculations for all the diketo tautomers were undertaken by the CNDO/2 method. The choice of this approach is justified by the following reasons:

i) Within the CNDO approximation the diketo tautomers of uracil and thymine were found to be energetically more stable by 43.4 and 49.2 kJ mol⁻¹, respectively, than the enol form [11]. This is in accordance with spectroscopic results [10, 12, 13], thus the preference of the diketo form is supposed for the other derivatives, too.

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ii) The calculated equilibrium geometries were found to be useful for the calculations of vibrational spectra at CNDO level [7].

iii) If the same empirical method is applied for the calculation of the geometries in a series of compounds with similar structures as the errors are (supposed to be) systematic, the relative changes in the geometries due to substitutions are expected to be correctly shown and so it is possible to draw conclusions on substitution effects.

Methods of calculation

The equilibrium geometry of a molecule is the configuration of nuclei where the molecular energy has a global minimum, *i.e.* where the acting nuclear forces (the negative gradients of energy with respect to nuclear coordinates) vanish and the matrix of force constants (second derivatives of energy) is positive definite.



Fig. 1. Calculated distances (in pm) and angles (in degrees) in uracil compared to X-ray diffraction data [4] (in parentheses)

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We applied PULAY's force method [1]: the first derivatives were calculated analytically and the second differentiation was numerical.

In the widely used iterative procedures for geometry optimization the nuclei are displaced in each step proportionally to the forces acting on them until the minimum of energy is reached. The method requires, in each step, the calculation of the energy involving a rather time-consuming SCF iteration. Taking advantage of NALEWAJSKI's algorithm [2], one can considerably reduce the computing time.



Fig. 2. Calculated equilibrium geometry of 1-Me-U. The values in parentheses are the corresponding calculated ones of uracil. When there is no difference between the calculated parameters of uracil and its derivative, the values of uracil are omitted. Distances in pm, angles in degrees

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Fig. 3. Calculated equilibrium geometry of 3-Me-U. For explanation of values in parentheses see legend of Fig. 2

12.55

Following NALEWAJSKI's method, the molecular lenergy can be expressed as $E = E(\mathbb{C}, r)$

where the parameters C are the LCAO MO coefficients in the SCF iteration and r contains the nuclear coordinates. It can be shown [2] that several nuclear configurations of different molecular energies can be attached to a given C^0 , *i.e.* to a given electronic distribution. Only one of these nuclear configurations $(r^0)^*$ has an energy (E^0) which is on the "real" energy surface (E) of the molecule, while the energies corresponding to the other nuclear configurations describe a "pseudo energy" surface:

$$E_1 = E_1(\mathbb{C}^0, r)$$

* Upper indexes correspond to the real energy surface, lower indexes to the pseudo energy surface.



Fig. 4. Calculated equilibrium geometry of 1,3-diMe-U. For explanation of values in parentheses see legend of Fig. 2

There is a minimum $[E_1^{\min}(\mathbb{C}^0, r_1)]$ on this pseudo energy surface and $E_1^{\min} < E^0$. The nuclear configuration (r_1) is closer to the equilibrium geometry (r^{eq}) than the starting configuration.

On the other hand $E_1^{\min} > E^1$, *i.e.* the minimum of the pseudo energy surface is above the "real" energy surface. To get the real value (E^1) for the molecular energy of $r_1(=r^1)$, one calculates the new electronic distribution $\mathbb{C}^1 \cdot E^1$ is much closer to the global minimum E^{eq} than the starting value E^0 and the local minimum E_1^{\min} . The process described above is repeated for \mathbb{C}^1 : the pseudo minimum $[E_2^{\min}(\mathbb{C}^1, r_2)]$ corresponding to this electronic distribu-

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tion yields the nuclear configuration r_2 , which is again closer to the equilibrium. After the calculation of \mathbb{C}^2 and E^2 the same process is repeated until the global minimum E^{eq} on the total energy surface is reached. Three or four steps are enough in general.

For testing purposes another type of calculations was also applied in our work: the "method of force relaxation" in which the information contained in the second derivatives is exploited [1]. Namely, having a configuration close to the equilibrium and a correct harmonic force field (\mathbf{F}_0), the necessary displacements (Δq) towards the equilibrium geometry are given, in one step, by:

$$\varDelta q = \mathbf{F_0^{-1}} \varphi_0$$

where q is the vector of internal coordinates and φ_0 that of the internal forces.



Fig. 5. Calculated equilibrium geometry of 5-Me-U (thymine). For explanation of values in parentheses, see legend of Fig. 2

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In the general case, \mathbf{F}_0 is approximately known and the energy surface is not harmonic, the optimum geometry cannot be reached in one step and the following iterative formula must be applied:

$$q_{i+1} = q_i + \mathbf{F}_0^{-1} \varphi_i$$

The correctness of the approximate force constants \mathbf{F}_0 influences the rate of convergence only, but not the final configuration. The correction of force constants during the procedure accelerates the convergence — generally three of four steps are enough [1]; the modified force constants due to the limited number of iterative steps, however, are still not accurate enough for all purposes (e.g. for the calculation of vibrational spectrum).



Fig. 6. Calculated equilibrium geometry of 6-Me-U. For explanation of values in parentheses, see legend of Fig. 2

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Fig. 7. Calculated equilibrium geometry of 5,6-di-Me-U. For explanation of values in parentheses, see legend of Fig. 2

Results and Discussion

The above calculation was applied to the methyl-substituted uraclis $(1-Me, 3-Me, 5-Me, 6-Me, 1,3-diMe, 5,6-diMe)^*$ and azauracils (5-aza and 6-aza). The results obtained are presented in Figs 1-9 and in Tables I and II. All distances are in picometers, all angles in degrees.

General remarks

The calculated geometric parameters of uracil are compared to X-ray diffraction data [4] in Fig. 1. Because of the inherent indeterminacies of both the calculated and experimental data used here for comparison, differences smaller than, say, 1.5° will not be discussed here.

* In all what follows the abbreviations U for uracil and Me for methyl will be used.

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Comparison of bond angles (in degrees)

				Cor	npounds+	+			
Angles+	n	I-Me-U	3-Me-U	5-Me-U	6-Me-U	1,3-diMe-U	5,6-diMe-U	5-aza-U	6-aza-U
Ring:									
$C_2 - N_1 - C_6$	121.7	119.7	121.7	121.8	124.3	119.8	124.0	120.7	125.9
$N_3 - C_2 - N_1$	114.9	116.2	116.1	114.3	115.0	116.9	114.3	113.4	114.5
$C_4 - N_3 - C_2$	126.2	126.1	124.2	126.1	125.2	124.5	125.6	124.7	123.6
$C_5 - C_4 - N_3$	115.5	115.0	116.6	117.2	115.5	116.2	117.1	119.3	114.1
$C_6 = C_5 - C_4$	119.3	119.4	119.3	116.3	122.0	119.0	118.7	-	123.7
$N_1 - C_6 - C_5$	122.4	123.5	122.0	124.2	118.0	123.5	120.3	126.3	-
$C_2 - N_1 - H_7$	118.8	_	118.7	118.7	116.9		117.4	119.2	119.9
$O_8 = C_2 - N_1$	121.9	121.5	120.9	122.1	121.5	120.8	122.2	122.4	121.3
${\bf H_9}\!-\!{\bf N_3}\!-\!{\bf C_2}$	115.7	116.0	-	116.1	116.5	-	116.4	117.3	117.2
$O_{10} = C_4 - N_3$	118.0	118.1	117.8	117.3	117.8	117.4	117.0	119.0	119.0
$H_{11} - C_5 - C_4$	119.1	119.0	119.0	_	117.6	119.3	- ,	_	120.3
$H_{12} - C_6 = C_5$	123.8	122.6	123.9	122.8		122.7	-	112.2	
$C_6 = N_5 - C_4$	-	-	—	—		-	-	115.6	—
$N_1 - N_6 = C_6$	-	-	_	-	—		—	-	118.2
C_{me_1} -ring	-	120.2	114.8	120.9	126.3	119.6	119.5	-	
C_{me_a} -ring	-	-	-	-	-	116.6	125.0	-	-
Substituent									
$H_{13} - C_{me_1} - ring$	-	111.1	111.0	113.3	113.0	111.0	113.1	-	-
$H_{14} - C_{me_1} - ring$	-	111.7	111.7	112.2	111.2	111.8	112.6	—	-
$H_{15}-C_{me_1}-ring$	-	111.7	111.7	112.2	111.2	111.8	112.6	-	-
$H_{13} - C_{me_1} - H_{14}$	-	107.4	107.5	106.4	107.3	107.5	106.1	-	-
$H_{13} - C_{me_1} - H_{15}$	-	107.4	107.5	106.4	107.3	107.5	106.1	-	-
$H_{16} - C_{me_2} - ring$	-	-	-	-	_	110.8	113.4	-	-
$H_{17}-C_{me_2}-ring$	-	_	-	-	-	111.9	111.1	-	-
$H_{18}-C_{me_2}-ring$	-	-	_	-	-	119.9	111.1	-	-
$H_{16} - C_{me_2} - H_{17}$	-	-	-	-	-	107.5	107.2	-	-
$H_{16} - C_{me_2} - H_{18}$	-	-	-	-	-	107.5	107.2	-	_

⁺ Numbers refer to indexes of atoms in Figs 1-9⁺⁺ Notations: U = uracil; Me = methyl; diMe = dimethyl

				Co	ompounds*	: #c			
Type of bond*	U	l-Me₌U**	3-Me-U	5-Me-U	6-Me-U	1,3-diMe-U	5,6-diMe-U	5-aza-U	6-aza-U
Ring:									
$N_1 - C_2$	138.4	138.7	138.5	138.2	138.4	138.9	138.2	138.4	138.2
$C_2 - N_3$	137.9	137.9	138.2	137.8	137.7	138.2	137.6	137.5	137.3
$N_3 - C_4$	138.9	139.0	139.5	139.0	139.1	139.6	139.0	138.9	138.6
$C_4 - C_5$	143.5	143.4	143.5	144.3	143.1	143.4	144.0	138.7	143.2
$C_5 = C_6$	134.3	134.3	134.3	135.2	135.6	134.3	136.6	130.5	130.4
$N_1 - C_6$	137.9	138.5	137.9	138.0	139.1	138.4	139.0	136.9	131.0
$N_1 - H_7$	106.4	-	106.5	106.4	106.6	_	106.5	106.5	106.8
$C_2 = O_8$	127.8	127.9	127.9	127.9	127.9	127.9	127.9	127.7	127.8
$N_3 - H_9$	106.7	106.7	-	106.7	106.6	_	106.6	106.5	106.7
$C_4 = O_{10}$	127.8	127.8	127.9	127.8	127.9	127.9	127.9	127.4	127.9
$C_5 - H_{11}$	111.2	111.3	111.3		111.4	111.3	-	_	111.2
$C_6 - H_{12}$	111.7	111.8	111.7	111.9	_	111.9	-	111.9	_
C _{ring} -C _{methyl}	-	-	_	145.8	145.3	-	145.9		-
		-	_	_	-	—	145.5	_	—
$N_{ring} - C_{methyl}$	_	141.0	-	_	_	141.0	_	-	_
	-	-	141.2	-	_	141.2	-	_	—
Substituent									
C _{methyl} -H _{methyl}	_	_	-	_	-	_	_	-	-
$C_{me_1} - H_{13}$	_	111.2	112.0	111.9	111.8	112.0	112.0	-	-
$C_{me_1} - H_{14}$	-	112.1	112.1	112.1	112.0	112.1	112.2	_	-
C _{me1} -H ₁₅	-	112.1	112.1	112.1	112.0	112.0	112.2	-	-
$C_{me_2} - H_{16}$	-	_	-	-	_	112.0	111.9	-	-
Cme2 -H17	-	-	-	-	_	112.0	112.0	-	-
$C_{me_2} - H_{18}$	-	-	_	_	_	112.0	112.0	_	_

Table II Comparison of bond lengths (in pm)

* Numbers refer to notations of Figs 1-9** Notations: Me = methyl; diMe = dimethyl

The relatively large differences in the calculated and experimental exoring bond angles may be an indication of the structural differences in the solid phase as compared to free molecules.

When discussing calculated bond lengths compared to the experiment, one has to consider that the CNDO values may be greater by 3-5 pm than



Fig. 8. Calculated equilibrium geometry of 5-aza-U. For explanation of values in parentheses see legend of Fig. 2

the best experimental parameters (obtained by microwave or electron diffraction spectroscopy) of equilibrium geometry for free molecules. This difference may increase when experimental values are taken from X-ray experiments, especially for the CH and NH bonds. Nevertheless, as shown in Fig. 1, experimental and calculated bond lengths in the ring agree satisfactorily, only those of CH, NH and CO, outside the ring, differ considerably.

In order to draw some conslusion on these bond lengths, we refer to the example of a qualitatively similar compounds: the simplest and hence most

studied molecule containing an O=C-N linkage, *i.e.* formamide. The comparison of bond lengths is presented in Table III. One can see that the X-ray values of N-H and C-H bonds in solid phase (1st column) differ as much from the gas phase values [experimental (2nd column) or calculated (3rd and 4th columns)] as in the case of uracil. It is to be remarked, however, that the X-ray values [14] for these bond lengths are very inaccurate and the real values in solid phase may differ from them. In the gas phase, on the contrary,

			(I)	
Bond type	X-ray diffraction data [4]	Gas electron diffraction data [15]	Ab initio calculations [14]	CNDO/2 calculations [16
N-H	91.0	102.7	102.0	106.9
C-H	88.0	112.5	110.0	112.2
C = 0	124.3	121.2	121.6	126.8

Table III

Characteristic bond lengths of formamide (in pm)

(the better accuracy of the experiments is improved by the agreement of gas electron diffraction [15] and *ab initio* data [14] for formamide.

On the other hand, the trend of change in the C=O bond length does not show the same regularity as those of N-H and C-H. The discussion is all the more interesting as important conclusions can be drawn for uracil. Bond lengths calculated by CNDO/2 exceed X-ray diffraction data equally for uracil and formamide. It is unfortunate that no gas electron diffraction and *ab initio* data are available for uracil.



Fig. 9. Calculated equilibrium geometry of 6-aza-U. For explanation of values in parentheses, see legend of Fig. 2

Because of the importance of the peptide linkage in biology, the C=0 bond length in formamide has been studied by several authors (e.g. [14, 15, 17]) and it was concluded that the value of 121.2 pm [15] characterizes the independent molecules in the gas phase, while that of 124.3 pm [14] the hydrogenbonded C=O in crystal phase. In the light of this the rather large values obtained by the CNDO/2 calculation (126.8 pm [16]) must be attributed to an error of the method. This error is systematic as the method yields as large values for the C=O bond lengths in formamide as in uracil and in its eight other derivatives (Table III and Figs 1-9).

This systematic character of the errors allowed the comparison of the present calculated geometrical parameters with those of other molecules calculated by the same (CNDO/2) method and permitted to draw some qualitative conclusions on the ring structure of the pyrimidine bases considered. The comparison of the data presented in Table IV shows that there is an ethene-like $C_5=C_6$ double bond and an ethane type C_4-C_5 single bond in uracil. The ring of uracil (and its derivatives considered here) were found to be planar however, the structure is basically different from the benzene-like pyrimidine (shown in Fig. 10). There is practically no conjugation in uracil and its derivatives; this statement is also supported by the small values of respective off-diagonal force constants [7]. Thus, the pyrimidine bases considered here have no pyrimidine structure.



Fig. 10. Calculated distances (in pm) and angles (in degrees) in pyrimidine [19]

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Table IV

Type of bond	Reference co	mpound	Ref.	Uracil
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138.0

131.0

126.8

[19]

[18]

[16]

134.3

127.8

Pyrimidine:

Formamide:

Ethene:

Comparison of some characteristic calculated bond lengths (in pm) to those of uracil (all calculations by the CNDO/2 method)

Furthermore, owing to the systematic character of the errors on the calculated values, a comparison within the series of uracil derivatives is also possible.

Comparison of calculated bond angles and bond lengths

Methyl substituted uracils

C - C

C = C

C = 0

It is well known that the substitution of a hydrogen by an electrondonating group induces a characteristic lengthening of the ring and the diminution of the bond angle at the point of substitution. This effect must be accompanied by other changes in the ring geometries in order to conserve ring planarity.

The effect of substitution, however, practically does not extend over the bonds and angles neighbouring the substitution. As can be seen in Tables I and II, the adjacent bonds and angles are the only affected ones.

N-methyl-substitution in uracil yields a change of -2.0 degrees in the bond angle at the point of substitution and +1.1 degrees in the adjacent angles; values which are slightly different in the disubstituted compounds (see 1-Me, 3-Me and 1,3-diMe in Table I). This change is accompanied by a lengthening of the bonds by 0.3-0.6 pm equally for the mono- or disubstituted derivatives (Table II).

Effects of C-methyl-substitution are not as regular as those of N-substitution. While the change in the $C_4C_5C_6$ bond angle due to C_5 -methylation of uracil amounts to -3.0 degrees [compare cols. of 5-Me-U (thymine) and uracil in Table I], this change is much larger for C_6 -methylation: -4.4 degrees (compare $\ll C_5C_6N_1$ for 6-Me-U and U in Table I). The neighbouring ring angles change by 1.7 degrees for thymine and by 2.7 degrees for 6-Me-U.

Of course, the larger the deformation, the larger the lengthening of the adjacent bonds: the double bond lengthens by 0.9 pm in the case of thymine and by 1.3 pm in the case of 6-Me-U, while the single bonds change by 0.8 pm (C_4C_5 bond for thymine) and 1.2 pm (N_1C_6 bond for 6-Me-U), respectively.

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Though the two C-methylations seem to be identical (both methylations take place on a double bonded C atom, see Figs. 5 and 6), the deformations due to Me-substitution are significantly different. The origin of this is that the C_5 and C_6 atoms are not identical, the total net charge on them is of opposite sign: C_5 is negative with -0.145 a.u. while C_6 is positive with 0.179 a.u. (Here we used our calculated values which are only slightly different from those of ref. [13].) The "negatively charged" C_6 is less influenced by the methyl group than the "positive" C_6 and the thymine ring endures smaller deformation relative to the uracil ring than that of 6-Me-U.

In the case of 5,6-diMe-U, disubstitution is supposed to result in a superposition of the above described effect. As the substitutions take place on adjacent atoms here, the changes in the *endo*-ring bond angles and ring bonds should be additive. For calculating then the substitution effects in 5,6-diMe-U by taking into account the above observations for monosubstitution, additive formulas could be used, *e.g.* for the ring angles:

$$\swarrow_{\mathbf{U}} + \varDelta \measuredangle_{[(5-Me-\mathbf{U})-\mathbf{U}]} + \varDelta \measuredangle_{[(6-Me-\mathbf{U})-\mathbf{U}]} = \measuredangle_{5,6-diMe-\mathbf{U}}$$

i.e., the new angle in 5,6-diMe-U is the sum of the original one in uracil and and the differences of angles caused by 5- and 6-methylations, resulting for the $C_4C_5C_6$ angle in

 $\label{eq:119.3} \begin{array}{ll} 119.3^\circ - \ 3.0^\circ + \ 2.7^\circ = \ 119.0^\circ \\ \\ \text{or for the $C_5C_6N_1$ angle in} & 122.4^\circ + \ 1.7^\circ - \ 4.4^\circ = \ 119.7^\circ. \end{array}$

The comparison of these values with those of Table I (118.7° and 120.3° -respectively) indicates that the changes in the bond angles due to dimethylation could be well predicted, showing the validity of the additivity of methyla, tion effects.

The additivity is also verified for the changes in the bond lengths as the length of the double bond can be correctly predicted: 134.3 + 0.9 + 1.3 == 136.5 pm vs. 136.6 pm in Table I.

Aza-uracils

Contrary to the methylation considered above, the replacement of a -CH= group by a nitrogen inside the ring means a rather drastic change in the ring itself. Due to this, a global distortion of the ring structure is expected. Surprisingly, however, the results show that the local deformations remain predominant. This might be connected with the isoelectronicity of the -N= and the -CH= groups.

The change of the C_5 -H group to N_5 for 5-aza-U and the C_6 -H one for N_6 in the case of 6-aza-U is entailed by a decrease of the angle by 3.7 and 4.2 degrees, respectively, at the point of substitution. The neighbouring angles increase by 3.8 and 3.9 degrees in 5-aza-U, while by 4.4 and 4.2 degrees in the 6-aza derivative.

As for the bond lengths, only three important changes can be observed with respect to uracil: those due to the replacement of the C=C bond by the C=N bond, the C-C by the C-N and the C_6 -N by the N-N bond. In Figs 8 and 9 the bond lengths of aza-uracils and uracil (in parentheses) are compared, while Table V shows the comparison of these bond lengths to characteristic bond lengths of other molecules.

Type of bond	Compound*	Reference	R (in pm)
C-N	Methylamine (Calc.)	[18]	140.0
	Pyrrole (Calc.)	[19]	138.2
	[Pyrrole (MW)]	[20]	(137.0)
CN	Pyridine (Calc.)	[19]	134.4
	[Pyridine (MW)]	[21]	(134.0)
	Pyrimidine (Calc.)	[19]	134.2
C = N	Methylenimine (Calc.)	[18]	128.0
	[N-Methylenimine (MW)]	[22]	(130.2)
C = N	[Acetonitrile (MW)]	[23]	(115.7)
$C_4 - N_5$	5-aza-U (Calc.)	Present	138.7
$C_4 - N_3$	5-aza-U (Calc.)	Present	138.9
$C_6 - N_1$	5-aza-U (Calc.)	Present	136.9
$C_6 = N_5$	5-aza-U (Calc.)	Present	130.5
$C_5 = N_6$	6-aza-U (Calc.)	Present	130.4
N-N	[Hydrazine (MW)]	[18]	(145.0)
	[Thiadiazole (MW)]	[24]	(137.1)
	Pyrazole (Calc.)	[19]	131.8
	Pyridazine (Calc.)	[19]	128.1
NN	[Pyridazine (MW)]	[25]	(133.0)
N = N	Azyne (Calc.)	[18]	122.0
	[Azomethane (ED)]	[26]	(124.7)
$N_6 - N_1$	6-aza-U (Calc.)	Present	131.0

Table V

	Comparison	of	C-N	and	N-N	bond	lengths	in	different	compounds
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* Calculated values are to be compared, experimental values are in parentheses Notations: ED = Gas electron diffraction

MW = Microwave spectroscopy

Calc. = Calculated values by the CNDO/2 method

In 5-aza-U, one can observe that a single C-N bond forms between the C_4 and N_5 atoms, the same type as that between N_3 and C_4 . (Its numerical value of 138.7 pm agrees well with the calculated 138.9 pm between N_3 and C_4 .) The comparison of this bond length to the calculated C-N bond in methylamine, 140.0 pm [18], shows that the C_4-N_5 and C_4-N_3 single bonds are only slightly conjugated. (Conjugated C-N bond lengths are less, about 134 pm; see calculated values for pyridine and pyrimidine in Table V and Fig. 10.) The C_6-N_1 bond is a little shorter (136.9 pm) than in U (137.9 pm) with a carbon atom (C_6) much more positively charged (see Table VI). The comparison of the bond length for $C_6=N_5$ (130.5 pm) to the calculated C=N bond length in methylenimine (128.0 pm [18]) proves that a double bond is present here.

The comparison of the C-N and N-N bond lengths in different compounds is presented in Table V. To draw qualitative conclusions, the values calculated by the same method were compared; nevertheless some experimental values are also listed in parentheses.

Though the same C=N bond length is calculated for 6-aza-U (130.4 pm), the effects of the substitution of C by N in the ring are different in this case. Here, the conjugation between the atoms 1 and 6 of the molecule is more pronounced (see Fig. 9): the N_1-N_6 bond length (131.0 pm) can be compared best to that of pyrazole (131.8 pm [19]) in Table V. This small conjugation of the N-N bond is accompanied by the fact that N_6 is positively charged (see Table VI). This "positivity" of N_6 and the small difference of total net charges between the atoms 5 and 6 in 6-aza-U (especially compared to the large difference in 5-aza-U, see Table VI) results in a weaker double bond in 6-aza-U than in 5-aza-U, though the length of the double bond is the same in both cases.

Based on the values of Table V, one is driven to the idea that the reactivity of these compounds will be different in the reactions of the double

Molecule	Atoms	Total net charge (a.u.)
Uracil	C ₅	-0.145
	C_6	0.179
5-aza-Uracil	N_5	-0.251
	C_6	0.251
6-aza-Uracil	C ₅	-0.045
	\mathbf{N}_6	0.026

Table VI

Total net charges by the CNDO/2 method for two characteristic atoms in the uracil ring

bond. This difference is observed indeed [27] but the fact that 5-aza-U shows no photoreactivity (in contrary to the other)s, could be explained on the basis of extended quantum chemical calculations only [6].

Conclusion

As is shown, substitution on the uracil ring is accompanied mainly by local effects contrary to e.g. the benzene ring, where methylation leads to changes in the structure spread all over the ring [28]. It seems that there are no general rules similar to those existing for some other types of rings and that each qualitatively different substitution on uracil must be investigated separately. This latter statement implies a criticism on a large number of theoretical papers publishing results on large and complicated systems of pyrimidine bases where no special attention is paid to the fine structure of the skeleton of uracil. It is reported, on the contrary, that rather small changes in the ring structure (e.g. those due to 6-methylation or 5-azatation) completely change the reactivity of uracils [6, 27]. We believe that the large variety of very different chemical, physical (and biochemical) properties of uracil derivatives is related to the substitution effects.

Finally, some remarks on the quantum chemical method we used *i.e.* on the CNDO/2 approximation. The reasons of our choice have already been listed in the introduction. In spite of recent criticism, this method remains widely used and is the only standard one applied rather systematically for a large number of molecular systems in order to predict very different properties.

The results presented in this work are self-explanatory and support the statement that despite of its low accuracy in determining some geometrical parameters of individual molecules, one may conclude that the CNDO/2 force method can be successfully used for interpretation of changes in the geometries for a molecular series.

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REACTIONS OF HAFNIUM TETRACHLORIDE WITH THIO-SCHIFF BASES DERIVED FROM S-METHYLDITHIOCARBAZATE

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The reactions of hafnium tetrachloride with thio-Schiff bases (derived from the condensation of S-methyldithiocarbazate with aldehydes/ketones) in different molar ratios have been carried out in refluxing dichloromethane. The products of the type, $HfCl_3(TSB)$, $HfCl_2(TSB)_2$ and $HfCl_2(TSB')$, $[TSB]^-$ and $[TSB']^{2-}$ are the anions of mono- and dibasic thio-Schiff bases, respectively were obtained and characterized on the basis of elemental analysis, electrical conductance measurements and spectral (infrared and electronic) data.

Introduction

In recent years, a large number of metal complexes of thio-Schiff bases containing NS or ONS donor atoms have been studied [1-10]. The increased interest in this field may be attributed to striking structural features and the reported carcinostatic and antiviral activity of NS and ONS donor ligands and their transition metal complexes [5, 6]. It has also been observed that a small structural change, such as the change of a substituent in the ligand may lead to an enhanced anticancer and antiviral activity of a transition metal complex [6]. ALI et al. [1-5] have investigated a series of metal chelates obtained from S-methyldithiocarbazate and its Schiff bases, and have also studied their anticancer activity. A survey of the literature revealed that no work has been carried out on the reactions of hafnium tetrachloride with Schiff bases derived from S-methyldithiocarbazate. With this view, it was considered worthwhile to study the reactions of hafnium tetrachloride with Schiff bases derived from S-methyldithiocarbazate.

The infrared spectral studies of the Schiff bases derived from S-methyldithiocarbazate have shown that in solid state these thio-Schiff bases exist in the thione form (I). However, in solution they undergo tautomerism. The thiol form (II) readily loses a proton on its reaction with a metal with the formation of a M-S bond [2].



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Table I

Reactions of hafnium tetrachloride with thio-Schiff bases in dichloromethane

Reactants (mole ratio)	Refluxing time (hours)	Product and colour	Analysis % found (calcd.)		
			Hf	C1	N
(1)	(2)	(3)	(4)	(5)	(6)
$\mathrm{HfCl}_4 + \mathrm{TSB}_1\mathrm{H} \ (1:1)$	48	HfCl ₃ (TSB ₁) Brown	37.09 (36.87)	21.77 (21.97)	6.07 (5.79)
$\mathrm{HfCl}_4 + \mathrm{TSB}_1\mathrm{H} \ (1:2)$	55	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{1})_{2}$ Brown	28.17 (27.55)	10.22 (10.94)	8.02 (8.65)
$\mathrm{HfCl}_4 + \mathrm{TSB}_2\mathrm{H} \ (1:1)$	50	HfCl ₃ (TSB ₂) Yellow	36.25 (36.12)	22.31 (21.52)	6.07 (5.67)
$\mathrm{HfCl}_{4} + \mathrm{TSB}_{2}\mathrm{H}\;(1:2)$	60	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{2})_{2}$ Yellow	26.38 (26.72)	10.30 (10.61)	8.02 (8.39)
$\mathrm{HfCl}_4 + \mathrm{TSB}_3\mathrm{H} \ (1:1)$	55	HfCl ₃ (TSB ₃) Orange-yellow	37.21 (37.80)	23.45 (22.53)	5.26 (5.93)
$\mathrm{HfCl}_4 + \mathrm{TSB}_3\mathrm{H}\ (1:2)$	65	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{3})_{2}$ Brown	28.80 (28.60)	$ \begin{array}{r} 11.42 \\ (11.36) \end{array} $	8.21 (8.98)
$\mathrm{HfCl}_4 + \mathrm{TSB}_4\mathrm{H} \ (1:1)$	55	$HfCl_3(TSB_4)$ Light-yellow	35.98 (36.71)	21.45 (21.88)	5.12 (5.76)
$\mathrm{HfCl}_4 + \mathrm{TSB}_4\mathrm{H} \ (1:2)$	60	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{4})_{2}$ Brown-yellow	26.77 (27.37)	$ \begin{array}{r} 10.32 \\ (10.87) \end{array} $	7.98 (8.59)
$HfCl_4 + TSB_5H (1:1)$	56	HfCl ₃ (TSB ₅) Yellow	34.66 (35.12)	20.29 (20.93)	4.88 (5.51)
$\mathrm{HfCl}_4 + \mathrm{TSB}_5\mathrm{H}\ (1:2)$	63	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{5})_{2}$ Yellow	25.96 (25.64)	10.75 (10.19)	7.86 (8.05)
$\mathrm{HfCl}_4 + \mathrm{TSB}_6\mathrm{H} \ (1:1)$	54	HfCl ₃ (TSB ₆) Yellow	30.65 (31.30)		4.42 (4.91)
$\mathrm{HfCl}_4 + \mathrm{TSB}_6\mathrm{H}\ (1:2)$	65	$\mathrm{HfCl}_{2}(\mathrm{TSB}_{6})_{2}$ Yellow	22.33 (21.76)	8.50 (8.64)	6.58 (6.83)
$\mathrm{HfCl}_4 + \mathrm{TSB}_1'\mathrm{H}_2$ (1 : 1)	50	HfCl ₂ (TSB ₁ ') Yellow	36.85 (37.68)	14.80 (14.97)	5.40 (5.91)
$\mathrm{HfCl}_4 + \mathrm{TSB}_2'\mathrm{H}_2$ (1 : 1)	54	HfCl ₂ (TSB ₂) Yellow	35.91 (36.60)	13.98 (14.54)	5.02 (5.74)

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Experimental

Materials

 HfCl_4 (Alpha Products) was used without any further purification. Dichloromethane (BDH) was dehydrated by refluxing it over phosphorous pentoxide and then finally distilled over anhydrous calcium chloride. S-methyldithiocarbazate was prepared by the method reported in the literature [11], and thio-Schiff bases were synthesised by the condensation of S-methyldithiocarbazate with the appropriate aldehyde/ketone in alcohol [6].

All operations were carried out under strict anhydrous conditions and a glass apparatus with standard interchangeable joints was used throughout the work.

Analytical methods

Hafnium was determined gravimetrically as HfO₂, and chlorine as AgCl.

Physical measurements

The infrared spectra of the complexes were recorded on a Perkin-Elmer 621 spectrophotometer in KBr pellets. Electrical conductance measurements in DMF were made on Elico Conductivity Bridge Type CM82T. Electronic and nuclear magnetic resonance spectra of the complexes were recorded on a Perkin-Elmer 4000A spectrophotometer and a Perkin-Elmer R32 spectrometer, respectively.

Reaction of hafnium tetrachloride with thio-Schiff base (molar ratio 1:1 and 1:2)

To the calculated amounts of $HfCl_4$ and thio-Schiff base dichloromethane (~ 60 mL) was added. The reaction mixture was then refluxed till the evolution of HCl gas ceased. After the completion of the reaction, the excess of the solvent was removed under reduced pressure to give the solid compound.

For the sake of brevity, the details of the reactions of $HfCl_4$ with different thio-Schiff bases are summarized in Table I.

Results and Discussion

A systematic study of the reactions of hafnium tetrachloride with monobasic thio-schiff bases (molar ratio 1:1 and 1:2) such as S-methyl- β -N--(furfurylmethylene)dithiocarbazate (TSB₁H), S-methyl- β -N(phenylmethylene) -dithiocarbazate (TSB₂H), S-methyl- β -N-(cyclopentyl)dithiocarbazate (TSB₃H) S-methyl- β -N-(cyclohexyl)-dithiocarbazate (TSB₄H), S-methyl- β -N-(phenylethylene)dithiocarbazate (TSB₅H) and S-methyl- β -N-(diphenylmethylene)dithiocarbazate (TSB₆H) in refluxing dichloromethane yielded the complexes of the type, HfCl₃(TSB) and HfCl₂(TSB)₂, according to the following equations:

$$\begin{split} \mathrm{HfCl}_{4} + \mathrm{TSB} \xrightarrow[\mathrm{CH_{2}Cl_{2}}]{} \mathrm{HfCl}_{3}(\mathrm{TSB}) + \mathrm{HCl}^{\uparrow} \\ \mathrm{HfCl}_{4} + 2 \operatorname{TSBH} \xrightarrow[\mathrm{CH_{4}Cl_{4}}]{} \mathrm{HfCl}_{2}(\mathrm{TSB}_{2}) + 2 \operatorname{HCl}^{\uparrow} \end{split}$$

where [TSB]⁻ represents the anion of the corresponding monobasic thio-Schiff base (TSBH).

These complexes are yellow to dark brown solids, and are insoluble in common organic solvents. Only few of them are soluble in dimethylformamide (DMF) and dimethylsulphoxide (DMSO). The electrical conductance measure-

ments of soluble complexes in dimethylformamide show them to be nonelectrolytes. All the complexes are susceptible to hydrolysis.

The reactions of hafnium tetrachloride with S-methyl- β -N-(2-hydroxyphenylmethylene)dithiocarbazate (TSB'₁H₂) and S-methyl- β -N-(2-hydroxyphenylethylene)dithiocarbazate (TSB'₂H₂) in 1 : 1 and 1 : 2 molar ratios in refluxing dichloromethane yielded only the complexes of the type, HfCl₂(TSB'), according to the following equation:

$$\mathrm{HfCl}_{4} + \mathrm{TSB'H}_{2} \xrightarrow{\mathrm{CH}_{2}\mathrm{Cl}_{2}} \mathrm{HfCl}_{2}(\mathrm{TSB'}) + 2 \mathrm{HCl}^{\uparrow}$$

where $[TSB']^{2-}$ represents the anion of the dibasic thio-Schiff base $(TSB'H_2)$.

These complexes are intense yellow solids and are highly hydrolysable in nature. They are insoluble in all the common organic solvents except dimethylformamide. The electrical conductance measurements in dimethylformamide show their nonelectrolytic nature.

The elemental analyses and physical data of the reaction products are given in Table I.

Infrared spectra

The infrared spectra of the thio-Schiff bases do not display a v(SH) band in the region $\sim 2500 \text{ cm}^{-1}$, indicating that in the solid state they remain in the thione form [6, 7]. This is further confirmed by the appearance of a band in the region $3290-3100 \text{ cm}^{-1}$ corresponding to the v(NH) vibrational mode. However, in the complexes this band disappears completely, indicating the deprotonation of the ligands on complexation [1-5]. The medium to strong band observed in the region $1655-1590 \text{ cm}^{-1}$ in these thio-Schiff bases is due to v(C=N) vibration of the azomethine group [12-14]. This band shifts by $\sim 50-15 \text{ cm}^{-1}$ in the spectra of the complexes and is observed in the region $1620-1555 \text{ cm}^{-1}$. The downward shift in v(C=N) vibration may be attributed to the lowering of the C=N bond order as a result of the coordination of the azomethine nitrogen to metal atom [12-14].

In the infrared spectra of the ligands, the four bands occurring in the regions 1485–1460, 1290–1210, 1075–1015 and 770–725 cm⁻¹ may be assigned to thioamide-I, -II, and -IV vibrations [15], respectively. These bands, assigned to thioamide vibrations are not pure but have substantial contributions of $\nu(C-N)$, $\delta(N-H)$, $\delta(C-H)$ and $\nu(C=S)$ vibrations, are found to be absent in the spectra of the complexes. The disappearance of thioamide bands along with the absence of $\nu(NH)$ band in the complexes indicates that the sulphur atom of the thiol group has taken part in bond formation with hafnium atom [16].

The infrared spectra of the dibasic thio-Schiff bases exhibit bands in the regions 3160-3100 and 1270-1270 cm⁻¹ attributable to v(OH) combined with v(NH), and v(C-O) (phenolic) vibrations [13, 14], respectively. In the

spectra of the complexes, the first band vanishes completely, while the second band shows an upward shift and is found in the region $1320-1300 \text{ cm}^{-1}$. These evidences thereby suggest the formation of M-O bond through deprotonation [13, 14]. The band sobserved in the regions 605-595 and 485-420cm⁻¹ can tentatively be assigned to v(Hf-N) and v(Hf-O) vibrations [16, 17], respectively. Similarly the bands appearing in the region $400-320 \text{ cm}^{-1}$ can be assigned to the mixture of v(Hf-S) [15] and v(Hf-Cl) [18, 19], vibrations however, specific assignments are difficult to make.

Electronic spectra

The electronic spectra of a few soluble complexes, recorded in dimethylformamide, show a single band in the region $27,700-26,500 \text{ cm}^{-1}$ which can be assigned to a charge-transfer transition.

In view of the insoluble nature of these complexes in almost all the common organic solvents, it appears that these complexes possess polymeric structures. It is suggested that the polymerisation can be attained through the bridge chlorine. However, the polymeric structures could not be confirmed by molecular weight determination in view of their insolubility in common organic solvents.



where $\langle N \rangle$ represents the anion of the bidentate monobasic thio-Schiff base.





Thus, on the basis of the elemental analyses, electrical conductance measurements and spectral data, the following structures can tentatively be assigned to the complexes, $[HfCl_3(TSB)]_n$ (A), $[HfCl_2(TSB)_2]_n$ (B) and $[HfCl_{2}(TSB')_{n}(C)]$.

Thus, the complexes obtained from bidentate ligands possess five- and six-coordinate stereochemistry, whereas the complexes obtained from tridentate ligands have five-coordinate stereochemistry. Similar type of structures have been reported with other metals [2, 4, 6].

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TRANSITION METAL CHEMISTRY OF OXIME CONTAINING LIGANDS, XVI

Fe(II) COMPLEXES OF QUINOLINE-2-ALDOXIME AND ISOQUINOLINE-3-ALDOXIME

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Iron(II) complexes of the type $Fe(HL)_2(X)_2$ [where HL = quinoline-2-aldoxime (HQOX) or isoquinoline-3-aldoxime (HIQOX) and $X = Cl^-$, Br^- , I^- , NCS⁻ or NCSe⁻] were synthesized and characterized by elemental analysis, molar conductance, molecular weight determination, X-ray powder diffraction patterns, magnetic susceptibility, Mössbauer, reflectance and IR spectral measurements. On the basis of these physical studies a halide bridged dimeric *cis*-octahedral structure is suggested for the iron(II) halide complexes, whereas the remaining complexes appear to be monomeric with a *cis*- octahedral structure.

Introduction

Aromatic aldoximes such as quinoline-2-aldoxime (HQOX) and isoquinoline-3-aldoxime (HIQOX) have structural features in common with ligands of both the 2,2'-bipyridyl and the dimethylglyoxime types. In spite of this obvious interest in the properties of molecules possessing two distinct types of coordination sites, very little work has been reported [1] on metal complexes of HQOX and HIQOX. For Fe(II) complexes studies have been mainly restricted [2] to complexes of pyridine-2-aldoxime, 6-methylpyridine--2-aldoxime, syn-phenyl-2-pyridylketoxime and syn-methyl-2-pyridylketoxime. The present paper reported on the synthesis and characterization of Fe(II) complexes of HQOX and HIQOX by physicochemical studies.

Experimental

Materials and Methods

Quinoline-2-aldoxime (HQOX) and isoquinoline-3-aldoxime (HIQOX) were prepared from 2-methylquinoline and 3-methylisoquinoline (K and K) Laboratories, New York) according to reported methods [3]. The authenticity of the compounds were established by means of their analysis and physical properties. The hydrated Fe(II) halide, potassium thiocyanate, potassium selenocyanate, 2,2-dimethoxypropane (K and K Laboratories) and other organic solvents of reagent grade.

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Preparation of the Complexes

Dihalo-bis(quinoline-2-aldoxime) iron(II) and dihalo-bis(isoquinoline-3-aldoxime) iron(II), Fe(HL)₂(X)₂ (HL = HQOX or HIQOX and X = Cl⁻, Br⁻ or I⁻)

 ${\rm FeX_2} \cdot 4$ H₂O (0.025 mol) was dissolved in a mixture of 20 mL ethanol and 25 mL 2,2-dimethoxypropane and refluxed for 30 min under a stream of N₂ gas atmosphere. A solution composed of HQOX or HIQOX (0.05 mol) in 25 mL of 1 : 1 (V/V)ethanol: 2,2-dimethoxypropane was heated to boiling and added dropwise with stirring to the metal halide solution under a N₂ gas atmosphere. A deep red colour was developed immediately and a deep red crystalline solid was formed with 3-5 min. The solid was filtered under N₂ atmosphere and was washed with ethanol and diethyl ether. The solid was dried over P₄O₁₀ in vacuum.

Di-isothiocyanato-bis(quinoline-2-aldoxime) iron(II) and di-isothiocyanato--bis(isoquinoline-3-aldoxime) iron(II); $Fe(HL)_2(NCS)_2$ (HL = HQOX or HIQOX)

 $Fe(NCS)_2$ (0.04 mol) in 25 mL ethanol, prepared metathetically from $FeCl_2 \cdot 4 H_2O$ and KSCN, was added dropwise with stirring under N₂ atmosphere to a hot solution of HQOX or HIQOX (0.08 mol) in 25 mL of ethanol. The mixture was refluxed for 2 hrs under N₂ atmosphere. On cooling the solution mixture at room temperature, a dark greenish-red crystalline solid was obtained which was filtered under N₂ atmosphere. The solid was washed with ethanol and diethyl ether and dried over P₄O₁₀ in vacuum.

Di-isoselenocyanato-bis(quinoline-2-aldoxime) iron(II) and di-isoselenocyanato--bis(isoquinoline-3-aldoxime iron(II), Fe(HL)₂(NCSe)₂ (HL = HQOX or HIQOX)

The procedure used in preparing these complexes was the same as that used to prepare $Fe(HL)_2(NCS)_2$ except that KSCN was used in place of KSeCN. The product was a dark red polycrystalline solid.

Physical Measurements

Conductance measurements were made on a Toshniwal conductivity bridge type CL 01/01. Molecular weights of complexes were determined cryoscopically. X-ray powder photographs were obtained using a Philips X-ray generator, nickel filtered copper radiation ($\lambda_0 = 1.5418$ Å) and a Debye Scherrer camera. Magnetic measurements from room temperature to 78 K were made on a standard Gouy balance, using CoHg(NCS)₄ as a calibrant. The diamagnetic corrections were estimated by using Pascal's constants. The room temperature magnetic moments are presented in Table I.

Iron-57 Mössbauer spectra were recorded on a polycrystalline solid by using a constant acceleration Mössbauer spectrometer. The spectrometer was equipped with a copper matrix source which was maintained at room temperature and was calibrated with a natural iron foil. The low temperature results were recorded in a vacuum cryostat with a sample holder which protected the sample from the cryostat vacuum. The results were determined by inspection with an accuracy of ± 0.01 mm/sec. The various Mössbauer parameters are presented in Table II.

Diffuse reflectance spectra were recorded at room temperature on a Cary 14 spectrophotometer equipped with a reflectance accessory, using MgO as a reference. The reflectance spectral data are reported in Table III. The infrared spectra of HQOX and HIQOX and their complexes in the $4000-200 \text{ cm}^{-1}$ range were recorded in CsI on a Perkin-Elmer 337 spectrophotometer and far-infrared spectra in the range $400-100 \text{ cm}^{-1}$ were recorded on a Fourier spectrophotometer (FS-30). The relevant IR spectral data are recorded in Table IV.

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Analytical and magnetic moment data for iron (11) complexes

Compound*	M W	Found (cale.) %					$\mu_{\rm eff}, \mu_{\rm B}$
	M. W.	С	н	N	Metal	X	299 °K
Fe(HQOX) ₂ (Cl) ₂	_	51.02 (50.97)	3.44 (3.39)	11.92 (11.89)	11.92 (11.85)	15.16 (15.08)	5.39
Fe(HQOX) ₂ (Br) ₂	_	42.88 (42.87)	2.92 (2.85)	10.02 (10.00)	10.08 (9.96)	28.62 (28.58)	5.42
Fe(HQOX) ₂ (I) ₂	_	36.79 (36.70)	2.50 (2.44)	8.52 (8.56)	8.69 (81.53)	38.94 (38.85)	5.50
$Fe(HQOX)_2(NCS)_2$	520.4 (515.8)	46.58 (46.53)	3.16 (3.10)	10.75 (10.85)	10.97 (10.81)	22.56 (22.49)	5.52
Fe(HQOX) ₂ (NCSe) ₂	615.2 (609.8)	43.34 (43.29)	2.67 (2.62)	13.80 (13.77)	9.25 (9.15)	25.27 (25.19) [‡]	5.50
Fe(HIQOX) ₂ (Cl) ₂	_	50.89 (50.87)	3.31 (3.39)	11.95 (11.89)	11.62 (11.85)	15.21 (15.08)	5.35
Fe(HIQOX) ₂ (Br) ₂	_	42.80 (42.87)	2.89 (2.85)	10.08 (10.00)	9.82 (9.96)	28.42 (28.58)	5.52
Fe(HIQOX) ₂ (I) ₂		36.72 (36.70)	2.43 (2.44)	8.59 (8.56)	8.42 (8.53)	38.78 (38.85)	5.56
Fe(HIQOX) ₂ (NCS) ₂	-	46.48 (46.53)	3.19 (3.10)	10.76 (10.85)	10.78 (10.81)	22.40 (22.49)	5.45
Fe(HIQOX) ₂ (NCSe) ₂	602.7 (609.8)	43.38 (43.29)	2.68 (2.62)	13.62 (13.77)	9.10 (9.15)	25.24 (25.19) [‡]	5.46

* HQOX = quinoline-2-aldoxime, $HIQOX = isoquinoline-3-aldoxime^{\ddagger}Se$

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Compound	T (K)	δ ^a (mm/sec)	${\it \Delta E_{ m Q}} \ ({ m mm/sec})$	Γ_1^{b} (mm/sec)	Γ_2^{b} (mm/sec)
$Fe(HQOX)_2(Cl)_2$	78 RT	$\begin{array}{c} 3.14\\ 2.80\end{array}$	$\begin{array}{c} 1.14 \\ 1.04 \end{array}$	$\begin{array}{c} 0.28\\ 0.28\end{array}$	$\begin{array}{c} 0.27\\ 0.28\end{array}$
$Fe(HQOX)_2(Br)_2$	78 RT	$\begin{array}{c} 3.12\\ 2.78\end{array}$	$\begin{array}{c} 1.16 \\ 1.06 \end{array}$	$\begin{array}{c} 0.26 \\ 0.24 \end{array}$	$\begin{array}{c} 0.24 \\ 0.24 \end{array}$
$Fe(HQOX)_2(I)_2$	78 RT	$\begin{array}{c} 3.10\\ 2.78\end{array}$	$\begin{array}{c} 1.14 \\ 1.06 \end{array}$	$\begin{array}{c} 0.25\\ 0.22\end{array}$	$\begin{array}{c} 0.24 \\ 0.23 \end{array}$
$Fe(HQOX)_2(NCS)_2$	78 RT	$\begin{array}{c} 3.08 \\ 2.74 \end{array}$	$\begin{array}{c} 1.12 \\ 1.02 \end{array}$	$\begin{array}{c} 0.26\\ 0.23\end{array}$	$\begin{array}{c} 0.24 \\ 0.24 \end{array}$
$Fe(HQOX)_2(NCSe)_2$	78 RT	$\begin{array}{c} 3.08\\ 2.75\end{array}$	$\begin{array}{c} 1.10\\ 1.05 \end{array}$	$\begin{array}{c} 0.27\\ 0.26\end{array}$	$0.25 \\ 0.25$
$Fe(HIQOX)_2(Cl)_2$	78 <i>RT</i>	$\begin{array}{c} 3.10\\ 2.75\end{array}$	$\begin{array}{c} 1.12 \\ 1.02 \end{array}$	$\begin{array}{c} 0.26 \\ 0.24 \end{array}$	$\begin{array}{c} 0.25\\ 0.24\end{array}$
$Fe(HIQOX)_2(Br)_2$	78 RT	$\begin{array}{c} 3.08 \\ 2.75 \end{array}$	$\begin{array}{c} 1.10\\ 1.02 \end{array}$	$\begin{array}{c} 0.24 \\ 0.24 \end{array}$	$\begin{array}{c} 0.26\\ 0.26\end{array}$
$Fe(HIQOX)_2(I)_2$	$78 \ RT$	$\begin{array}{c} 3.10\\ 2.80\end{array}$	$\begin{array}{c} 1.10\\ 1.00 \end{array}$	-0.27 0.28	$\begin{array}{c} 0.26\\ 0.26\end{array}$
$Fe(HIQOX)_2(NCS)_2$	$78 \ RT$	$\begin{array}{c} 3.07\\ 2.70\end{array}$	$\begin{array}{c} 1.08 \\ 0.99 \end{array}$	$\begin{array}{c} 0.26\\ 0.26\end{array}$	$\begin{array}{c} 0.25\\ 0.24\end{array}$
$Fe(HIQOX)_2(NCSe)_2$	$78 \ RT$	$\begin{array}{c} 3.09 \\ 2.70 \end{array}$	$\begin{array}{c} 1.07\\ 1.00\end{array}$	$\begin{array}{c} 0.24\\ 0.24\end{array}$	$\begin{array}{c} 0.24 \\ 0.23 \end{array}$

Table II

Mössbauer spectral parameters

 a Relative to natural iron foil b Full width at half-maximum for low velocity line, \varGamma_1 and highvelocity line, \varGamma_2

Reflectance spectral data (cm^{-1})				
Compound	${ m Fe}(t_{2g}) o \pi^*({ m HL})$	${}^5B_2 \rightarrow {}^5B_1$	${}^5B_2 o {}^5A_1$	
$Fe(HQOX)_2(Cl)_2$	18.940	10.400	8.410	
$Fe(HQOX)_2(Br)_2$	18.900	10.800	8.600	
$Fe(HQOX)_2(I)_2$	18.860	12.000	9.600	
$Fe(HQOX)_2(NCS)_2$	19.200	12.140	-	
Fe(HQOX) ₂ (NCSe) ₂	19.250	12.160	_	
$Fe(HIQOX)_2(Cl)_2$	18.940	10.415	8.440	
Fe(HIQOX) ₂ (Br) ₂	18.950	10.670	8.650	
Fe(HIQOX) ₂ (I) ₂	18.900	12.100	9.720	
Fe(HIQOX) ₂ (NCS) ₂	19.260	12.16	_	
Fe(HIQOX) ₂ (NCSe) ₂	19.300	12.200		

Table III

Results and Discussion

The Fe(II) ion, on interaction with HQ OX and HIQOX, yields complexes corresponding to the general formula $Fe(HL)_2(X)_2$ (HL = HQOX or HIQOX and X = Cl⁻, Br⁻, I⁻, NCS⁻ or NCSe⁻). All the complexes are quite stable at room temperature and do not show any sign of decomposition even after long standing. All the complexes are insoluble in water and non-polar solvents and, except for Fe(II) halo complexes, p artially soluble in moderately polar solvents and soluble in polar solvents. The molar conductance of $Fe(HL)_2$ (X)₂ (HL = HQOX or HIQOX and X = NCS⁻ or NCSe⁻) complexes in nitrobenzene and in ethanol (~ 10⁻³ M) determined at 27 °C indicate their non-electrolytic behaviour [4]. Molecular weights of $Fe(HL)_2(X)_2$ (HL = HQOX or HIQOX and X = NCS⁻ or NCSe⁻) in formamide show that they are monomeric.

The X-ray powder diffraction results* suggest that is othio yanate and isoseleno yanate complexes of the same ligands are X-ray isomorphous, whereas the halo complexes are not isomorphous with any one of the complexes mentioned above and hence, are structurally different.

The Fe(II) complexes exhibit [5] slightly temperature dependent magnetic moments in the 5.50 to 5.38 $\mu_{\rm B}$ range, which are characteristic values for tetragonally distorted, octahedral, high-spin Fe(II) complexes. The very small temperature dependence ($\sim 3 \%$ or less) indicates that the ground term is split to the extent of 1000 cm⁻¹ or more [6].

The room temperature Mössbauer chemical isomer shift values, δ , relative to a natural iron foil, which is sensitive to both the oxidation state and spin-state of iron, are of the magnitude expected [7] for distorted octahedral, high-spin Fe(II) complexes and show a slight increase with decreasing temperature. The increase in chemical isomer shift values, δ , with decreasing temperature can be attributed to the second-order Doppler shift arising from lattice effects and are indicative of a low Debye temperature for these Fe(II) complexes. The chemical isomer shift values, δ , are surprisingly constant from one anion to the next and indicate that a change in the anion group with its varying electron donating power has little effect upon the s-electron density at the surface of the iron nucleus in the present Fe(II) complexes.

The magnitude and temperature dependence of the quadrupole splitting, $\Delta E_{\rm Q}$, reported in Table II is also that which is expected for tetragonally distorted high-spin, octahedral Fe(II) complexes. It is interesting to note that the temperature dependence of the quadrupole splitting is large and of the same order of magnitude in Fe(II) complexes. This temperature dependence [7, 8] of $\Delta E_{\rm Q}$ is an indication of an electric field gradient which is a thermal average of gradients resulting from the occupation of two or more orbital states.

* The X-ray powder diffraction results can be had from the author on request.

Compound	ν(C—N)	ν (N—O)	u(Py=I)	$\nu(\mathrm{Py}\mathrm{-II})$	v(Py-III)	v(Py—IV)	γ (C—H)
ноох	1520(m)	980(vvs)	1580(vs)	1550(s)	1465(s)	1420(s)	788(s, b)
Fe(HQOX) ₂ (Cl) ₂	1620(m)	1050(s)	1590(vs)	1570(s, sh)	1470(s) 1460(vs)	1435(s)	820(s) 800(w)
$Fe(HQOX)_2(Br)_2$	1610(s, sh)	1067(s)	1590(vs)	1570(sh)	1470(s) 1460(vvs)	1440(vs)	820(s) 805(sh)
$Fe(HQOX)_2(I)_2$	1618(s, sh)	1070(s)	1600(vs)	1570(w,sh)	1480(s) 1460(vvs)	1440(vs)	815(m) 800(w)
$Fe(HQOX)_2(NCS)_2$	1610(s)	1054(s)	1590(vs)	1560(sh)	1472(s) 1450(vvs)	1440(vs)	820(s) 800(sh)
$Fe(HQOX)_2(NCSe)_2$	1610(sh)	1060(vvs)	1600(vvs)	1565(sh)	1480(vs) 1460(vvs)	1442(vs)	820(s) 804(sh)
HIQOX	1518(m)	980(vvs)	1575(vs)	1550(vs)	1460(s)	1425(s)	780(s)
$Fe(HIQOX)_2(Cl)_2$	1618(m)	1060(vs)	1600(vs)	1570(vs)	1470(s) 1460(vs)	1440(s)	818(s) 800(w)
$Fe(HIQOX)_2(Br)_2$	1615(s, sh)	1068(m)	1595(s)	1560(w)	1472(s) 1460(vvs)	1435(vs)	820(s) 800(w)
$Fe(HIQOX)_2(I)_2$	1619(s, sh)	1070(s)	1590(vs)	1570(sh)	1475(s) 1460(vvs)	1440(vs)	820(s) 800(w)
$Fe(HIQOX)_2(NCS)_2$	1616(sh)	1070(vvs)	1600(vs)	_	1480(s) 1460(vs)	1442(s)	818(vs) 800(m)
$Fe(HIQOX)_2(NCSe)_2$	1618(sh)q	1070(vvs)	1600(vs)	-	1480(s) 1465(vvs)	1440(vs)	818(vvs) 800(m)

Table IV

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Compound	$\varphi(C-C)$	Ligand absorption bands	$ u({ m Fe}{-\!\!-\! m X}) $	$ u({ m Fe}-N)$ ligand
HQOX	742(s)	400(s) 390(s), 290(m), 270(m), 220(m) 185(s, b), 185(s, b), 120(s, sh)	_	_
$Fe(HQOX)_2(Cl)_2$	775(s), 760(s)	400(s), 390(s), 295(w) 250(m)	230(m), 215(w)	370(s), 350(w)
	742(s)	220(w), 185(m), 125(s)	170(w)	320(s) 280(m)
$Fe(HQOX)_2(Br)_2$	775(s), 760(s)	400(s) 295(w), 248(m)	140(w)	370(m), 350(m)
	745(s)	220(w), 187(m), 127(s)	110(w)	318(m), 280(w)
$Fe(HQOX)_2(I)_2$	775(s), 760(m) 740(vs)	398(s), 390(m), 290(m), 250(m) 220(m), 185(m), 120(m)	-	370(s), 350(s) 318(m), 280(w)
$Fe(HQOX)_2(NCS)_2$	775(s), 758(m)	400(s), 385(m), 290(m), 250(s)	320(s), 240(m)	370(m), 350(s)
	745(vs)	220(m), 185(m), 125(m)	200(m), 170(w)	316(m), 280(w)
$Fe(HQOX)_2(NCS)_2$	775(s), 758(m)	398(s), 390(m), 290(m), 220(m)	300(vs), 245(m)	370(s), 350(m)
	745(vvs)	190(s), 125(s)	210(m), 180(w)	315(sh), 280(m)
HIQOX	740(s)	400(s), 380(s), 292(m), 224(m) 180(s), 125(w)	-	—
$Fe(HQOX)_2(Cl)_2$	775(s), 760(m)	400(s), 295(m), 225(m)	240(s), 215(w)	368(s), 350(m)
	748(w)	182(m), 125(s)	175(w)	320(s), 280(w)
$Fe(HIQOX)_2(Br)_2$	770(s), 760(s)	395(s), 390(m), 297(m), 220(s)	135(w)	370(vs), 359(w)
	745(m)	185(m), 125(m)	110(w)	318(m), 218(s)
Fe(HIQOX) ₂ (I) ₂	770(s), 760(s) 740(m)	400(s), 390(m), 292(m), 220(s) - 185(m), 127(s)	—	370(vs), 340(w) 320(sh), 278(s)
$Fe(HIQOX)_2(NCS)_2$	765(s), 758(m)	395(s), 390(m), 295(m), 225(s)	320(s), 250(m)	370(vs), 350(m)
	742(s)	185(m), 125(s)	210(m), 175(m)	314(sh), 280(m)
$Fe(HIQOX)_2(NCSe)_2$	768(s), 760(m)	400(s), 385(m), 295(m), 220(s)	320(s), 238(m)	368(vs), 348(s)
	740(s)	182(s), 120(w)	208(w), 170(w)	310(sh), 280(m)

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Then, as a consequence, the temperature dependence may indicate a splitting of the ground state t_{2g} orbitals of the octahedral Fe(II) ion by the lower symmetry components of the ligand field.

The diffuse reflectance spectra of all the Fe(II) complexes are somewhat similar to one another and suggest a distorted ligand field geometry around the Fe(II) atom. In halo complexes the immediate geometry around the Fe(II) atom is four nitrogen atoms and two halogen atoms arranged in a *cis*octahedral structure (see far IR spectra). Therefore, the sharp spectral bands observed in the 8210-9720 and 10,400-12,100 cm⁻¹ range can be assigned [9] to ${}^{5}B_{2} \rightarrow {}^{5}A_{1}$ and ${}^{5}B_{2} \rightarrow {}^{5}B_{1}$ transitions, respectively, which result from the splitting of the ${}^{5}E_{g}$ excited state (O_{h} symmetry) in C_{2v} symmetry. It is apparent that the splitting of the ${}^{5}E_{g}$ excited state (O_{h} symmetry) is of the order of 2000 to 2400 cm⁻¹ in these complexes.

The isothiocyanate and isoselenocyanate Fe(II) complexes also exhibit spectra typical of *cis*-octahedral complexes, except that the splitting of the band is not observed and a single sharp band is observed at $\sim 12,160 \text{ cm}^{-1}$. This situation is certainly consistent with the structures of these Fe(II) complexes. In isothiocyanate and isoselenocyanate complexes, the Fe(II) atom is coordinated to six nitrogen atoms, which substantially reduces the asymmetry of the ligand field than the coordinated four nitrogen and two halogen atoms about the Fe(II) atom in the Fe(II) halo complexes.

HQOX and HIQOX exhibit multiple bands over the range of $3220 - 2810 \text{ cm}^{-1}$ which are assigned [2] to the intermolecular hydrogen bonded OH of the NOH groups. The v(C-H) stretching vibration which could be present in this region, is obscured by v(OH) absorption bands. The spectra of all the Fe(II) complexes exhibit strong bands in the 3480-3400 and $3050-3040 \text{ cm}^{-1}$ range which are assigned [2] to the free v(OH) of NOH groups and the v(C-H) stretching vibration of the ligand molecules, respectively. The v(C=N) acyclic and v(N-O) stretching vibrations in free HQOX and HIQOX are observed [2] at ~ 1520 and 980 cm^{-1} respectively. These stretching vibrations are shifted towards higher frequencies and appear at ~ 1620 and $\sim 1070 \text{ cm}^{-1}$, respectively, which is an indication [2] of the neutral oxime group ($\supset C=NOH$) coordinated to the Fe(II) atom in these complexes. The coordination of the pyridine nitrogen atom to the Fe(II) atom is indicated by shifting and splitting of the ring vibrations as is usually observed [10] for other metal(II) pyridine complexes.

In Fe(II) complexes very strong bands are observed at ~ 2070 and $\sim 2020 \text{ cm}^{-1}$, which are assigned to the $v_1[v(C-N)$ stretching] vibration of N-bonded thiocyanate or selenocyanate groups. The observed splitting of v_1 vibration is an indication [11] of a *cis*-configuration in these complexes. The v_2 [δ (NCS) or δ (NCSe)] and $v_3[v(C-S)$ or v(C-Se)] stretching vibrations are obscured by ligand absorption bands.

In $Fe(HL)_{o}(Cl)_{o}$ (HL = HOOX or HIQOX) complexes the bands at \sim 240 m and \sim 210 w cm⁻¹ are assigned to ν (Fe–Cl) stretching vibrations and at ~ 170 w to $\nu(\text{Fe}-\text{Cl})$ bending vibrations. In the case of Fe(HL)₂(Br)₂ complexes the bands due to $\nu(\text{Fe}-\text{Br})$ are weaker and appear at ~ 140 w and $\sim 110 \text{ w cm}^{-1}$. The bands due to $\nu(\text{Fe}-\text{I})$ are, as usual, weaker and no definite assignment of the $\nu(\text{Fe}-I)$ is possible in $\text{Fe}(\text{HL})_{0}(I)_{0}$ complexes. The relatively low frequency assigned [12] to these ν (Fe-halo) vibrations is consistent with a halogen bridging structure, although ν (M-halo) frequencies are observed over a wide range and some terminal ν (M-halo) frequencies are also reported in this region. In all these complexes four stretching vibrations of varying intensities associated with $\nu(\text{Fe}-\text{N})$ ligand vibrations are observed at \sim 370, \sim 355, \sim 320 and \sim 280 cm⁻¹, and vFe-NCS) and v(Fe-NCSe) stretching vibrations are also observed at \sim 320, \sim 240, \sim 200 and \sim 170 cm⁻¹ in the same region. These assignments are tentative because of the possibility of accidental coincidences and intensity variations, nevertheless the number of bands appear consistent [13] with cis-halogen coordination rather than trans. The similarity of v(Fe-N) ligand vibrations shows that in all these complexes the two ligand molecules have the same configuration in relation to each other.

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HETEROCYCLES FROM THIENOYL PROPIONATE, XI Synthesis of new pyridazine, cyclic hydrazide and Arylacetic acid derivatives of anticipated antimicrobial properties

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While ethyl β -aroylpropionate reacts with succinic ester to give unexpected cyclic products [1] thienoyl propionate gives the normal half-ester **1a**. Utilization of **1b** in the preparation of substituted[acids, anhydrides, lactones, cyclic hydrazides and pyridazine derivatives is described.

Substituted pyridazine, hydrazide and arylacetic acid derivatives useful as analgesic, antipyretic and anti-inflammatory agents can be obtained according to the scheme outlined in the chart, through a new route. As previously described [1], ethyl β -aroylpropionate gave cyclic ketones when condensed with succinic ester. For this purpose we allowed now methyl β -thienoylpropionate to react with dimethyl succinate. Surprisingly, the reaction gave a crude non-ketonic, acid material. A white crystalline solid separated from this oil on alkaline hydrolysis. The substance behaved as a tricarboxylic acid. The mass spectrum exhibited a prominent molecular ion peak at m/e 284. With acetyl chloride the product yielded the corresponding cyclic anhydride 2, which exhibited the expected carbonyl coupling bands in the IR spectrum. When treated with aluminium chloride in nitrobenzene, the anhydride 2, underwent ring closure to give the corresponding indenone (3a). Analytical data, IR and UV are clearly in accord with the bicyclic system 3, possessing the exocyclic double bond. The NMR spectrum also supported structure 3 displaying a simple two-proton thiophene absorption with doublet at 7.19 (J = 5 Hz) and 7.70 (J = 5 Hz), in addition to methylene protons for acetic 0

 $(-CH_2-C-)$ and propionic acids $(-CH_2-CH_2-C-)$. Upon treatment with methyl isocyanate, the oxime **3b** afforded the carbamate **3c**. The affinity of **1** and **2** to form cyclic hydrazide **4a** with hydrazine hydrate was displayed in ethanol at room temperature. The IR spectra had bands at 3400, 1700, 1660 and 1620 cm⁻¹. The reaction with dimethyl sulfate [2] and methyl isocyanate to form dimethyl and dicarbamate succinhydrazide derivatives (**4b** and **4c**) were also considered. The structural features of the carbamate are such as to make them suitable for testing as insecticides which may act as their own synergists [3]. For **4b** the NMR spectrum revealed signals due to methyl



resonance, in addition to propionic acid methylene protons. It also showed heterocyclic and carboxylic protons (see Experimental). Attempts to generate the unstable diacyl derivative were unsuccessful.

The base-catalyzed reaction of 4a with aldehydes gave 5. The IR spectrum showed the absence of NH bands. The NMR spectrum revealed no imino protons, but =C-H singlet was observed in addition to the previously mentioned methylene protons. This reaction is of interest, since it affords evidence that the transformation of the six into the five-membered ring occurs in all cases probably through molecular rearrangement involved in the mechanism.



With cinnamaldehyde further condensation at the double bond arrests the normal ring change with the appearance of additional vinylic protons in the NMR spectrum of 6.

It was found that attempted bromination of **lb** in acetic acid gave a substance which behaved as a dicarboxylic acid, as shown by anhydride formation. The IR spectrum had an additional lactone band, and on the bases of chemical analysis, NMR and mass spectra, the possible structure is 7, which compound was also obtained upon treatment with a mixture of hydrobromic acid, acetic acid and water. It is known that if the double bond of an unsaturated acid is farther down the carbon chain than between the alpha and beta positions, conjugate addition is not possible. Nevertheless, the double



bond and carbonyl group interact in the presence of acidic catalyst, because the carbocation that results from the addition of a proton to the double bond has a built-in nucleophile (the carboxyl group) which may attack the cationic centre to form a cyclic product, probably the lactone 7.

With compounds 7 and 8, hydrazine hydrate gave 9, as shown by the correct analytical data, IR and mass spectra.

Acid-mediated cyclization of the phenylsuccinopyrazolinepropionic acid 6 to the ring cyclized product 10 was effected using polyphosphoric acid [4], but yields were low.

Experimental

M.p.'s are uncorrected. IR spectra (KBr, ν max, cm⁻¹) were recorded on a Beckman IR 4220 spectrophotometer and electronic spectra (methanol, λ max, nm) on a Beckman UV 5230 spectrophotometer. Mass spectra were obtained on a Varian MAT 112. The NMR spectra were determined in deuteriochloroform at a frequency of 60 MHz on a Varian EM-360 spectrometer, using tetramethylsilane as internal standard. The peak positions are expressed in ppm (δ).

Stobbe condensation

A mixture of methyl β -thienoylpropionate (0.1 mol) and dimethyl succinate (0.14 mol) in *t*-butanol (15 mL) was gradually added during 30 min to a stirred solution of potassium *t*-butoxide [prepared from potassium (2.5 g) and *t*-butanol (60 mL)] at room temperature. The reaction mixture was stirred for 1 h, and then worked up as usual [5]. The oily product obtained (1a; 75%) failed to solidify.

IR: 1715 and 1685 (vC=0).

Upon saponification with 10% ethanolic sodium hydroxide, followed by trituration with ether *n*-hexane, the tricarboxylic acid (1b; 63%) precipitated, m.p. 208-210 °C (from benzene).

IR: 1700 - 1690 (broad) ($\nu C = O$).

C12H12O6S. Caled. C 50.70; H 4.22; S 11.26. Found C 51.12; H 3.98; S 10.76%.

Dehydration of acid 1b: formation of anhydride 2

Acid 1b (2 g) was refluxed with acetyl chloride (60 mL) for 2 h. The solution was then concentrated under reduced pressure. The resulting yellow anhydride (2) was crystallized, from benzene; m.p. 173-175 °C (55%).

IR: 1820 and 1760 (vC=0).

C12H1005S. Calcd. C 54.13; H 3.75; S 12.03. Found C 53.87; H 3.54; S 11.68%.

4(H)-0x0-5-carboxymethyl-cyclopenta[b]thiophene-6-propionic acid (3a)

To a cold and stirred mixture of anhydrous aluminium chloride in carbon disulfide the anhydride 2 (3 g) was gradually added at such a rate that the temperature of the mixture did not exceed 5 °C. The reaction mixture was kept at this temperature for 3 h and then at room temperature for 2 days with occasional stirring. Carbon disulfide was removed and the product decomposed as usual. The residue was extracted with alkali and the extract washed with ether and acidified. The product thus obtained was filtered off, washed with cold water, dried and crystallized from benzene-methanol to give 3a (2 g), m.p. 123-124 °C.

IR: 1740, 1690 (broad).

UV: 235, 330 (e, 13,000 and 15,000).

NMR (DMSO): δ 2.63 (2H, $-CH_2-COOH$), 3.55 (4H, $-CH_2-CH_2-COOH$), 7.19–7.7 (d, -CH=CH- thiophene, J = 5 Hz, AB system), 10.4 (1H, COOH), 11.65 (1H, COOH). $C_{12}H_{10}O_5S$. Calcd. C 54.13; H 3.75; S 12. 03. Found C 54.51; H 3.71; S 12.66%.

Reaction of the ketone 3a with hydroxylamine: formation of 3b

A suspension of 3a (2 g) and hydroxylamine hydrochloride (0.5 g) in a mixture of pyridine (1 mL) and ethanol (25 mL) was refluxed for 3 h. After cooling, the product was filtered off, dried and crystallized from methanol to obtain colourless crystals of 3b, m.p. 151 °C in 50% yield.

IR: 3400 and 1700.

 $\rm C_{12}H_{11}O_5NS.$ Calcd. C 51.24; H 3.91; N 4.98; S 11.38. Found C 50.88; H 4.12; N 5.32; S 11.59%.

Reaction of oxime 3b with methyl isocyanate: formation of 3c

A mixture of the oxime 3b (1 g), methyl isocyanate (0.2 mL) and triethylamine (2 drops). in dry benzene (20 mL) was refluxed for 5 h. The solvent was evaporated under reduced pressure and the oily residue obtained was washed with *n*-hexane and then triturated with methanol to obtain the methylcarbamate (3c) as colourless crystals, m.p. 203 °C (from benzene).

IR: 3320, 1700 and 1665.

 $\rm C_{14}H_{14}O_6N_2S.$ Calcd. C 49.70; H 4.14; N 8.28; S 9.46. Found C 50.12; H 4.22; N 7.76; S 9.91%.

Reaction of 1b with hydrazine hydrate: formation of the cyclic succinhydrazide derivative 4a

To a solution of 1b (0.01 mol) in absolute ethanol (30 mL), hydrazine hydrate (0.01 mol) in ethanol (10 mL) was gradually added dropwise, with stirring. The white precipitated product was left in ice overnight, then filtered off and crystallized from methanol to give 4a, m.p. 186-188 °C (70%).

IR: 3380 (broad) 1700 and 1640.

C12H12O4N2S. Calcd. C 51.42; H 4.28; N 10.0; S 11.42. Found C 51.56; H 4.56; N 10.50; S 11.89%.

Reaction of the anhydride 2 with hydrazine hydrate: formation of 4a

The anhydride 2 in ethanol was treated with hydrazine hydrate as above to give the cyclic hydrazide 4a in 75% yield, m.p. 190 °C. On admixing with a sample obtained by the hydrazine treatment of 1b, the m.p. was not depressed. The IR spectral bands for both substances were identical.

Reaction of the hydrazide 4a with dimethyl sulfate: formation of 4b

A solution of dimethyl sulfate (0.04 mol) in 75 mL of 50% ethanol was added, with stirring, over a period of 10 h, to a refluxing solution of the hydrazide 4a (0.01 mol) in 50% alcohol (60 mL). At the end of the reaction time the alcohol was evaporated, during which water was added to replace the alcohol. The remaining aqueous solution was extracted several times with chloroform and the combined extracts were dried over anhydrous sodium sulfate to give 4b (25%), m.p. 128 °C (from hexane chloroform). .0 -C-), 2.45 (2H, CH₂-C-),

IR: 1720 and 1635 ($\nu C = O$). NMR (DMSO): δ 2.1 (4H, A_2B_2 system

$$\operatorname{m}, -\operatorname{CH}_2 - \operatorname{CH}_2 - \operatorname{O}$$

3.15 (3H, CH₃-N), 3.35 (3H, CH₃-N), 3.92 (3H, C-OCH₃), 7.2 (thienyl protons). C15H1804N2S. Calcd. C 55.90; H 5.59; N 8.69; S 9.93. Found C 56.11; H 5.53; N 8.32; S 10.35%.

Reaction of 4a with methyl isocyanate: formation of 4c

A solution of 4a (1.5 g), methyl isocyanate (1 mL) and triethylamine (2 drops), in dry benzene (10 mL) was refluxed for 5 h. The solution was evaporated to dryness, and the oily residue washed with benzene several times and crystallized from acetic acid to give the dicarbamate 4c as colourless crystals, m.p. 253-255.°C; yield 1.1 g.

IR: 3350 (broad), 1710 (broad) and 1680 (broad).

C16H18O6N4S. Calcd. C 48.73; H 4.56; N 14.21; S 8.12. Found C 49.12; H 4.55; N 14.15; S 8.23%.

Reaction of 4a with aldehydes: formation of 5

A solution of the appropriate aldehyde (0.005 mol) in ethanol (5 mL) was added dropwise to a cold and stirred solution of the hydrazide (4a). (0.005 mol) in ethanol (10 mL) and 10% sodium hydroxide solution (5 mL). The resulting vellow product was allowed to stand in an ice bath overnight, then acidified, filtered off and crystallized from the proper solvent.

(a) Reaction of 4a with benzaldehyde: formation of 5a

The product obtained was crystallized from methanol to give yellow crystals, m.p. 136 °C, yield 82%. 0 0

IR: 1705 and 1620.

NMR (CDCl₂): d2.15 (4H, A2B2 system CH2-CH2-C-), 2.4 (2H, CH3-C-), 3.7 (1H, CH=N-), 7.12 (3H, thienyl protons), 7.65 (5H, ph-) 11.56 (1H, COOH).

C19H16O4N2S. Calcd. C 61.95; H 4.34; N 7.60; S 8.69. Found C 62.22; H 4.33: N 8.00; S 8.55%.

(b) Reaction of 4a with anisaldehvde: formation of 5b

The product obtained was crystallized from dilute methanol to give yellow crystals, m.p. 150 °C, in 85% yield. IR: 1700 and 1625.

NMR (CDCl₃): δ 2.33 (4H, A_2B_2 system, $CH_2 - CH_2 - C_-$), 2.55 (2H, CH_2) -). 3.5 (1H, CH=N-), 3.95 (3H, Ph-OCH₃), 6.95 (3H, thienyl protons), 7.7 (5H, Ph-), 10.85 (1H. COOH).

C20H18O5N2S. Calcd. C 60.30; H 4.52; N 7.03; S 8.04. Found C 60.55; H 4.59; N 6.59; S 7.68 %.1

(c) Reaction of 4a with thienaldehyde: formation of 5c

The product obtained was crystallized from chloroform to give yellow crystals, m.p. 121 °C, in 75% yield. IR: 1705 and 1630.

C17H14O4N2S2. Calcd. C 54.54; H 3.74; N 7.48; S 17.11. Found C 54.55; H 3.54; N 7.59; S 16.85%.

(d) Reaction of 4a with furfural: formation of 5d

The product was crystallized from dilute methanol to give yellow crystals of 5d, m.p. 115 °C (70% yield). IR: 1700 and 1620.

C17H14O5N2S. Calcd. C 56.98; H 3.91; N 7.82; S 8.93. Found C 57.25; H 4.11; N 8.13; S 9.22%.

(e) Reaction of 4a with cinnamaldehyde: formation of 6

The product was crystallized from chloroform to give yellow crystals of 6, m.p. 200-202 °C, in 80% yield.

IR: 1705, 1660 and 1620.

NMR (DMSO) δ 2.1 (4H, A_2B_2 system $CH_2 - CH_2 - C'_-$), 2.55 (2H, $CH_2 - C'_-$), 5.23 (br., 1H, d, CH-Ph, J = 6 Hz), 6.1–6.7 (m, 2H, CH=CH), 6.8 (3H, thienyl protons). C₂₁H₁₇O₄N₂S. Calcd. C 64.12; H 4.32; N 7.12; S 8.14. Found C 63.87; H 4.59; N 6.68; S 8.59%.

Attempted bromination of 1b: formation of 7

Bromine (0.02 mol) in glacial acetic acid (10 mL) was added dropwise at 0-5 °C to a solution of the acid 1b (0.01 mol) in acetic acid (20 mL) After 1h, the reaction mixture was poured into crushed ice, and the precipitated white solid was filtered off and crystallized from dilute acetic acid to obtain the lactone 7 in 68% yield, m.p. 180 °C.

IR: 1785 and 1700 (broad).

NMR (CDCl₃): δ 1.95 (4H, m, CH₂-CH₂-C, A_2B_2), 3.72 (ABX pattern for the $CH-CH_2-$ group of protons; $J_{AX}=J_{BX}$ 8 Hz, CH_2) and 4.85 (t, -CH-), 6.86 (3H, thienyl protons), 10.57, 11.15 (-COOH).

C12H12O6S. Calcd. C 50.70; H 4.22; S 11.26. Found C 50.58; H 4.41; S 10.89%.

Lactonization of la: formation of 7

The half-ester la (2 g) was refluxed for 10 h with a mixture of hydrobromic acid and water (20 mL, 2:1). At the end of the reaction, the solid which separated was taken up in ether and the ethereal layer extracted thoroughly with 10% sodium carbonate solution. The alkaline solution was acidified to give an acidic, colourless solid which was crystallized from dilute acetic acid in 52% yield, m.p. 175-178 °C. The substance gave no depression on admixture with compound 7 previously obtained. The IR spectral bands of both substances were identical.

Dehydration of the diacid 7: formation of the anhydride 8

The diacid 7 (2 g) was refluxed with acetyl chloride (60 mL) for 2 h. The solution was then concentrated under reduced pressure. The product failed to solidify. IR: 1810, 1785 and 1725.

Reaction of the diacid 7 with hydrazine hydrate: formation of the hydrazide 9

To a solution of 7 (0.01 mol) in absolute ethanol (30 mL), hydrazine hydrate (0.01 mol) in ethanol (10 mL) was added dropwise, with stirring. The white product which precipitated was allowed to stand in an ice bath overnight, then filtered off and crystallized from benzene methanol to give 9, m.p. 163 °C.

IR: 3350 (broad), 1670 (broad) and 1620.

C12H14O3N4S. Calcd. C 48.97; H 4.76; N 19.04; S 10.88. Found C 49.33; H 4.51; N 18.69; S 11.52%.

Reaction of the anhydride 8 with hydrazine hydrate: formation of 9

The anhydride 8 was treated with hydrazine hydrate as above, whereupon compound 9 deposited (m.m.p.).

Treatment of the phenylsuccinopyrazoline-propionic acid 6 with polyphosphoric acid: formation of 10

Polyphosphoric acid (40 g) was warmed to 80 °C and 2 g of 6 was added slowly, with mechanical stirring. The resulting mixture was heated at 80 °C for 2 h and then cooled and poured into ice-water, with vigorous stirring. After standing overnight, the product obtained was extracted with ether. The combined extracts were washed with sodium bicarbonate, dried over sodium sulfate and concentrated. The residue solidified on cooling to give yellow needles, m.p. 177 °C, (from benzene n-hexane).

IR: 1700 and 1620.

C21H15O3N2S. Calcd. C 67.20; H 4.00; N 7.46; S 8.53. Found C 67.31; H 4.52: N 7.93: S 8.98%.

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SYNTHESIS OF A-*NOR*-5-AZACHOLESTANE DERIVATIVES

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T we routes to A-nor-5-azacholestane derivatives from the unsaturated lactam 1 are described.

In our previous paper [1] we described an efficient synthesis of A-nor--B-homo-5-azacholest-6-en-3-one (1).

Contraction of ring B in this compound is the subject of the present contribution [2].

The oxidation of compound 1 with osmium tetroxide afforded the lactamodiol 2 [1]. Further oxidation with periodic acid resulted in the formation of the B-seco-aldehyde 3. Intramolecular condensation of 3 proceeding during heating in dioxane solution with concentrated hydrochloric acid yielded the unsaturated lactam 4 with the normal size of ring B.

Alkaline hydrolysis of the seco-aldehyde 3 also provided a product with 6-membered ring B, 6β -hydroxy-A-nor-5-azacholestan-3-one (6), probably via the intermediary compound 5. When the hydrolysis was followed by acidification of the reaction mixture, the main product was A-nor-5-azacholest-6-en--3-one (7). The minor product was the hydroxylactam 6. It was also proved that compound 6 under acidic conditions underwent partial dehydration (the reaction is reversible [1]) to give the unsaturated lactam 7. In the equilibrium state the ratio of compounds 7:6 was about 4:1.

An alternative route to indolizidine azasteroids consists in a rearrangement of the lactamodiol 2 under basic conditions. On heating 2 in boiling dioxane with aqueous KOH, formation of the isomeric diol 10 took place. It seems that in the first step of the reaction the open-chain structure 8 had formed; the isomerization of 8 via the common enolic form to ketone 9, followed by N-cyclization, afforded the lactamodiol 10.

Periodic acid oxidation of 10 yielded A-nor-5-azacholestan-3,6-dione (11). The same compound was obtained from the hydroxylactam 6 by ruthenium tetroxide oxidation.

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The lactamodiol 10 in THF solution treated with a drop of HClO₄ underwent dehydration to give the unsaturated alcohol 12. Compound 12 when allowed to stand in dioxane with hydrochloric acid isomerized slowly to 6ξ-formyl-A-nor-5-azacholestan-3-one (13).

The compounds described above will be subjected to biological investigations.

Experimental

M.p.'s were determined on a Koffler apparatus of Boetius type and are uncorrected. The measurements of optical rotation were performed on a Perkin-Elmer 241 polarimeter in CHCl_a. IR spectra were recorded on IR-20 and Unicam SP 1100 spectrophotometers in CHCl₃ or in KBr. UV spectra were taken on a Specord UV-VIS spectrophotometer in ethanolic solutions. ¹H-NMR_i spectra were obtained on a Jeol-100 apparatus in CDCl₃ with TMS $(\delta = 0 \text{ ppm})$ as internal standard. 6β , 7β -Dihydroxy-A-nor-B-homo-5-azacholestan-3-one (2) was synthesized according to the method previously described by us [1].

Cleavage of lactamodiol 2 by periodic acid

The lactamodiol 2 (1 g) dissolved in THF (150 mL) was treated with a saturated aqueous solution of $H_{r}IO_{c}$ (4 g). The reaction mixture was allowed to stand for 30 min at room temperature. The organic solvent was evaporated under reduced pressure at room temperature and the residue was extracted with carbon tetrachloride. The extract was washed with water, dried (anhydrous Na₂SO₄) and the solvent evaporated. The seco-aldehyde 3 obtained (970 mg) did not exhibit any tendency to crystallization. However, this material was essentially pure and was used in the further transformations; $[\alpha]_{25}^{25} + 69.5^{\circ}$ (c 1.0).

IR $(p_{\text{max}}^{\text{CHCla}})$: 2731 (CHO), 1741, 1721 and 1701 cm⁻¹ (C=O). | ¹H-NMR: δ 9.79 (m, w/2 = 5 Hz, 1H, -CHO), 8.95 (s, 1H, HCO-N-CO-), 1.55 (s, 3H, 19-CH₃), 0.75 (s, 3H, 18-CH₃).

UV: $\lambda \max 226 \operatorname{nm} (\varepsilon = 8900)$.

C26H42NO2 (417.63). Calcd. C 74.78; H 10.38; N 3.35. Found C 74.63; H 10.44; N 3.26%.

Closure of ring B in the seco-aldehyde 3

To a solution of the seco-aldehyde 3 (150 mg) in dioxane (30 mL) conc. hydrochloric acid (4 mL) was added. The reaction mixture was refluxed for 20 min, poured into water and extracted with benzene. The washed and dried (anhydrous Na₂SO₄) extract was evaporated and the residue crystallized from methanol - water. Yield of unsaturated lactam 4 was 95 mg, m.p. 117 - 119 °C, $[\alpha]_{\rm D}^{17} + 92.5^{\circ}$ (c 0.8).

IR $(\nu_{\text{max}}^{\text{CHCl}_{a}})$: 2730 (CHO), 1713 and 1681 (C=O), 1611 cm⁻¹ (C=C).

¹H-NMR: δ 9.31 (s, 1H, -CHO), 7.36 (s, 1H, 6-H), 1.17 (s, 3H, 19-CH₃), 0.94 (s, 3H, 18-CH₃).

UV: λ max 291 nm (ε = 14,700).

C28H41NO2 (399.62). Calcd. C 78.15; H 10.34; N 3.50. Found C 78.00; H 10.51; N 3.55%.

Synthesis of 6β -hydroxy-A-nor-5-azacholestan-3-one (6)

To a solution of the seco-aldehyde 3 (450 mg) in dioxane (30 mL) potassium hydroxide (600 mg) in water (3 mL) was added and the reaction mixture was refluxed for 2 h. After cooling, the reaction mixture was poured into water (200 mL) and extracted with benzene. The extract was washed, dried (anhydrous Na_2SO_4) and the solvent evaporated. The product, hydroxylactam 6, precipitated from hexane as an amorphous solid (290 mg), $[\alpha]_{D}^{25} + 17.9^{\circ}$ (c 1.0).

. IR $(\nu_{\text{max}}^{\text{KBr}})$: 3370 (O-H), 1697 cm⁻¹ (C=O).

¹H-NMR: δ 5.54 (m, w/2 = 9 Hz, 1H, 6 α -H), 4.97 (s, 1H, -OH), 1.43 (s, 3H, 19-CH). 0.84 (s. 3H. 18-CH.).

C₂₅H₄₅NO₂ (389.63). Calcd. C 77.07; H 11.12; N 3.59. Fond C 76.92; H 11.25; N 3.56%

Dehydration of the hydroxylactam 6

(a) The above hydroxylactam (100 mg) was dissolved in THF (5 mL), one drop o perchloric acid was added and the reaction mixture was allowed to stand for 0.5 h. It was then poured into water (100 mL) and extracted with CCl₄. Silica gel (70-270 mesh) chromatography of the crude material afforded A-nor-5-azacholest-6-en-3-one (7) (65 mg) and the starting hydroxylactam 6 (14 mg).

(b) The seco-aldehyde 3 (970 mg) was dissolved in dioxane (60 mL), a solution of KOH (1 g) in water (5 mL) was added and the reaction mixture was refluxed for 2 h. After cooling. conc. hydrochloric acid (3 mL) was added, the reaction mixture was poured into water (100 mL) and extracted with CCl₄. The extract was washed with water, dried (anhydrous Na, SO₄), evaporated and chromatographed on a silica gel (70-270 mesh) column. Elution with benzene — ether mixture (85:15) gave the unsaturated lactam 7 (680 mg), m.p. 102-103 °C (from aqueous acetone), $[\alpha]_{D}^{17} - 30.4^{\circ}$ (c 1.0).

 $\begin{array}{l} \text{IR } (p_{\max}^{\text{CHCl}_3}): 1682 \ (\text{C}=\text{O}), \ 1648 \ \text{cm}^{-1} \ (\text{C}=\text{C}). \\ {}^{1}\text{H-NMR: } \delta \ 6.69 \ (\text{dd}, \ J_{6-7}=8 \ \text{Hz}, \ J_{6-8}=3 \ \text{Hz}, \ 1\text{H}, \ 6\text{-H}), \ 4.94 \ (\text{dd}, \ J_{6-7}=8 \ \text{Hz}, \ J_{7-8}=2 \ \text{Hz}, \ 1\text{H}, \ 7\text{-H}), \ 1.08 \ (\text{s}, \ 3\text{H}, \ 19\text{-CH}_3), \ 0.72 \ (\text{s}, \ 3\text{H}, \ 18\text{-CH}_3). \end{array}$

UV: $\lambda \max 247 \text{ nm} (\epsilon = 16,400).$

C25H41NO (371.61). Calcd. C 80.80; H 11.12; N 3.77. Found C 80.68; H 11. 13; N 3.62%. With benzene — ether mixture (6:4) the more polar product, hydroxylactam 6, was eluted (185 mg). It precipitated from hexane as an amorphous solid.

Rearrangement of the lactamodiol 2

To a solution of the lactamodiol 2 (300 mg) in dioxane (30 mL) potassium hydroxide (200 mg) in water (8 mL) was added and the reaction mixture was refluxed for 2 h. After cooling the reaction mixture was diluted with water and extracted with benzene. The extract was washed, dried (anhydrous Na₂SO₄) and the solvent evaporated. The residue was crystallized from acetone. Yield of the isomeric dial 10 was 255 mg; m.p. 190-192 °C, $[\alpha]_{19}^{19}-11.0^{\circ}$ (c 0.91).

IR $(v_{\text{max}}^{\text{KBr}})$: 3305 (0-H), 1670 cm⁻¹ (C=O).

¹H-NMR: δ 5.46 (dd, $J_{H_A-OH} = 12$ Hz, $J_{H_B-OH} = 4.5$ Hz, 1H, O–H), 3.83 (dd, $J_{H_A-H_B} = 12$ Hz, $J_{H_B-OH} = 4.5$ Hz, 1H, –CH_AH_B–OH), 3.12 (t, $J_{H_A-H_B} = J_{H_A-OH} = 12$ Hz, 1H, –CH_AH_B–OH), 1.46 (s, 3H, 19-CH₃), 0.86 (s, 3H, 18-CH₃); the unusually well resolved O-H signal at δ 5.46 disappeared upon shaking the sample with D_2O and at the same time the methylene protons gave a normal AB system.

C₂₆H₄₅NO₃ (419.65). Calcd. C 74.42; H 10.81; N 3.34. Found C 74.17; H 10.82; N 3.36%

Reaction of the diol 10 with periodic acid

The diol 10 (100 mg) dissolved in freshly distilled THF (8 mL) was treated with a solution of H_5IO_6 (100 mg) in water (0.5 mL). The reaction mixture was allowed to stand for 1 h, p oured into water (100 mL) and extracted with benzene. The dried extract (anhydrous Na_2SO_4) was concentrated and the oily residue chromatographed on a silica gel (100-200 mesh)column. With benzene - ether mixture (7:3) A-nor-5-azacholestan-3,6-dione (11) was eluted (41 mg), m.p. 159 °C (from acetone). $[\alpha]_{19}^{D} + 36.1^{\circ}$ (c 1.0). The IR spectrum of 11 was identica with that described previously [3]. ¹H-NMR: δ 1.36 (s, 3H, 19-CH₃), 0.80 (s, 3H, 18-CH₃).]

Oxidation of the hydroxylactam 6 by ruthenium tetroxide

A mixture of NaIO₄ (2 g) in water (25 mL), CCl₄ (25 mL) and hydrated RuO₂ (10 mg) was shaken until the black precipitate completely dissolved. To the above oxidation mixture a solution of the hydroxylactam $\hat{\mathbf{6}}$ (100 mg) in CCl₄ (10 mL) was added dropwise during 15 min with vigorous shaking. Shaking was continued for further 15 min and then the lower, yellow

layer was separated. Several drops of isopropanol were added to decompose RuO4 and the black precipitate of RuO₂ was filtered off. The filtrate was dried (anhydrous Na₂SO₄) the solvent evaporated and the residue crystallized from acetone. The product obtained, imide 11, was identical with the compound described above (yield 59 mg).

Dehydration of the diol 10 under acidic conditions

The lactamodiol 10 (120 mg) was dissolved in freshly distilled THF (10 mL) and a drop of perchloric acid was added. The reaction mixture was allowed to stand for 30 min and then poured into water (100 mL) and extracted with benzene. The extract was washed with water, dried (anhydrous Na_2SO_4) and the solvent evaporated. The crude product 12 crystallized from acetone (yield 75 mg), m.p. 133–142 °C, $[\alpha]_{1^{19}}^{1^{19}}$ –23.4° (c 0.8). IR ($\nu_{\text{max}}^{\text{KBr}}$): 3431 (O–H), 1686 (C=O), 1650 cm⁻¹ (w, C=C). ¹H-NMR: δ 4.80 (s, 1H, 7-H), 3.80–4.20 (m, 3H, -CH₂–OH), 1.14 (s, 3H, 19-CH₃),

0.76 (s, 3H, 18-CH₂). After shaking the sample with D_2O the methylene protons gave a normal AB system at $\delta 4.05$ (2d, $J_{H_A-H_B} = 12.5$ Hz, 2H, $-\mathring{C}H_AH_B-OD$). UV: $\lambda \max 244$ nm ($\varepsilon = 14,780$).

C₂₆H₄₂NO₂ (401.64). Calcd. C 77.75; H 10.79; N 3.49. Found C 77.49; H 10.89; N 3.40%

Isomerization of the unsaturated alcohol 12

The unsaturated alcohol 12 (50 mg) in dioxane (5 mL) solution was treated with conc. hydrochloric acid (1 mL) and the reaction mixture was allowed to stand for 12 h. The usual work-up followed by crystallization from hexane afforded the lactamoaldehyde 13 (28 mg), m.p. $129 - 132 \,^{\circ}C$, $[\alpha]_{D}^{17} - 54.6^{\circ}$ (c 0.74).

IR $(\nu_{\text{max}}^{\text{KBr}})$: 2713 (CHO), 1738 and 1697 cm⁻¹ (C=O).

¹H-NMR: δ 9.45 (s, 1H, -CHO), 4.60 (m, w/2 = 12 Hz, 1H, 6-H), 1.14 (s, 3H, 19-CH₂), 0.73 (s, 3H, 18-CH₃).

C₂₆H₄₃NO₂ (401.64). Caled. C 77.75; H 10.79; N 3.49. Found C 77.47; H 10.82; N 3.49%.

Direct transformation of the lactamodiol 2 into aldehyde 13

To a solution of the lactamodiol 2 (150 mg) in dioxane (15 mL) potassium hydroxide (200 mg) in water (4 mL) was added and the reaction mixture was refluxed for 2 h. After cooling, the above mixture was treated with conc. hydrochloric acid (2.5 mL), let to stand for 12 h, poured into water (200 mL) and then extracted with benzene. The dried (anhydrous Na₂SO₄) extract was evaporated and the oily residue crystallized from hexane (yield of lactamoaldehyde 70 mg), m.p. $129 - 132 \,^{\circ}\text{C}$, $[\alpha]_{\text{D}}^{17} - 54.6^{\circ}$.

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THE MASS SPECTRA OF NITROGEN-CONTAINING STEROIDS, I

17- AND 17a-AZASTEROIDS AND STEROIDAL ALKALOIDS

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The mass spectrometric behaviour of seventeen models of the title compounds has been investigated in compraison with the analogous normal steroids. A dominating role of the basic nitrogen atom in directing the fragmentation of these types of compounds has been established, leading to a very selective decomposition and low molecular ion stability.

As experience with some derivatives has shown, the decreasing of the basicity of the nitrogen atom by introducing appropriate substituents and/or the presence of other charge localizing centres in the molecules result in more informative spectra displaying different fragments formed via decomposition of the steroidal skeleton itself.

In the case of the steroidal alkaloids investigated it has also been shown that, besides some similarity to the analogous steroidal sapogenins, there are interesting new fragmentation routes and, furthermore, acylation of the nitrogen atom provides a possibility to distinguish between the stereoisomeric pairs with different spiro-junction

Introduction

During the last two decades, a vast amount of knowledge concerning the mass spectrometry of normal steroids has accumulated. Steroids with the main types of skeleton and having various substituents (such as OH, OR, oxo, *etc.* groups) in different positions have been studied systematically, and correlations between these structures and their electron impact induced decompositions are now well documented [*e.g.* 1-4], helping to solve structural problems in this field.

In contrast, most of the mass spectra of nitrogen-containing steroids (amines, azasteroids, and steroidal alkaloids), which are of growing pharmaceutical importance, were merely reported for the sake of structural identification, and only few papers deal with the interpretation of the fragmentation in some detail.

A survey of the literature on the mass spectrometry of azasteroids (*i.e.* compounds containing nitrogen atom in the steroidal skeleton) affords an interesting picture about the influence of the nitrogen atom on the mass spectrometric behaviour.

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PANDIT et al. studied the fragmentation processes of 6-azaequilenin and 6-aza-14 β -isoequilenin [5], and they found the mass spectra of these compounds similar to those of equilenin and 14β -isoequilenin, which have no nitrogen atom in the skeleton: i.e. the nitrogen atom did not affect the fragmentation of these compounds. This seems to be connected with the fact that in the 6-azaequilenin isomers the nitrogen atom is a part of a stable aromatic system. In accordance with this, for some steroids bearing nitrogen atoms in a saturated ring system, the fragmentation patterns show interesting differences between the mass spectra of the azasteroids and those of their normal analogues. This can be seen from the mass spectra of some 6-azacholestanes, and 6-azaandrostanes (KUTNEY et al. [6]) and those of some lactams having a nitrogen atom in different (2-, 3-, 16-, 17-, 6-, or 6a) positions of the steroid skeleton (APLIN et al. [7], AHMAD et al. [8, 9]). A marked effect of the nitrogen atom on the fragmentation processes was observed by BARANOWSKA et al. in the mass spectra of 9-azasteroids [10] and by VERCHERE et al. for 8,13-diazaestranes [11]. The fragmentation pattern was highly susceptible to the presence of a nitrogen hetero atom in position 7 in the case of 6,7-diazaequilenins, according to POLLMANN's study [12].

As far as the literature of steroidal alkaloids is concerned, only some mass spectral data have been reported [13, 14], and no publication deals with their mass spectrometric behaviour.

From the above-mentioned literature it can be concluded that the presence of a nitrogen atom in several types of steroidal skeleton and in various positions has different effects and may cause a great selectivity in the fragmentation routes. This selectivity leads to a less informative mass spectrum, and hence makes structural analysis more difficult.

The aim of this work is to study the role of the nitrogen atom in the electron impact induced fragmentation of some 17-aza- and 2-(4'-methyl-1'--piperazino)-17a-azasteroids and steroidal alkaloids and, furthermore, to investigate how this role can be influenced by changing the basicity of the N-atom *via* derivatization. The results may help to elucidate structural problems of compounds of this type by mass spectrometry.

Results and Discussion

The model compounds investigated, the results and discussions are presented in three separate paragraphs of this paper, according to the different groups of the compounds.

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1. 17-azasteroids

The following androstane and estrane derivatives were examined:



The mass spectra of 3β -hydroxy-17-aza- 5α -androstane (Ia) and its derivatives (Ib, c) are shown in Fig. 1, together with that of 3β -hydroxy- 5α -androstane.

As can be seen, the abundance of the molecular ion of this latter compound is significant and the fragmentation of the steroidal skeleton gives rise to several abundant fragment ions (their origins are indicated in the structural formula in the Figure). Contrary to this, in the case of **Ib**, the molecular ion shows a much decreased stability and the mass spectrum is very simple: the only abundant peak exhibited corresponds to the $(M-CH_3)^+$ ion, arisen by the splitting off of a methyl group from the C_{18} position of the molecule (β cleavage to the N atom) and having an immonium cation structure, which is too stable to decompose.

The mass spectrum of Ic exhibited one more peak $(m/z \ 262)$ besides the molecular ion and the ion $(M-CH_3)^+$. Metastable observation supported that this ion was formed from the $(M-CH_2)^+$ ion by loss of a ClCH=CO molecule.

On the basis of these observations it can be concluded that for Ia-Ic the only main reaction centre of the fragmentation is the nitrogen atom.

The mass spectra of 17-azaestrone derivatives (IIa-c) having aromatic A ring are shown in Fig. 2, together with that of 3-methoxy-estra-1,3,5(10)--trien-17-one, published earlier [15]. Because of the presence of the aromatic A ring, this latter compound gave a stable molecular ion (base peak), and abundant peaks corresponding to the decomposition of the estrone skeleton



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(e.g. ions at m/z 160, 173, 186 and m/z 199 arisen via bond ruptures in the D or/and C rings, as shown in the Figure).

At the same time, IIa behaves similarly to Ia-c: the base peak corresponds to the $(M-CH_3)^+$ ion, and the molecular peak is weak, *i.e.* the N atom is again the main centre directing the fragmentation. The aromatic A ring stabilizes only an ion at m/z 173 with medium abundance. IIb decomposes to several fragments under electron impact, and at the same time the stability of its molecular ion is enhanced. The ion current carried by fragment ions due to decomposition of the steroidal skeleton is higher than 20% of the total. The large differences between IIa and IIb are due to the presence of 16-oxo group in the latter, which decreases the basicity and thereby the probability of charge localization on the nitrogen atom. Hence the aromatic A ring can acquire a role in directing the fragmentation and stabilizing the ions at m/z 160, 173, 186 and 110. (This latter is a complementary ion of m/z 160 originating from the $(M-15)^+$ ion.) The mass spectrometric behaviour of IIb suggests that the nitrogen atom and the aromatic ring are competing reaction centres during the fragmentation. The mass spectrum for compound IIc shows a molecular peak of less abundance than that in case of IIb, and only the ions at m/z 160 and 173 can be observed from the formerly mentioned series. This is attributed to the fact that the chloroacetyl group present does not decrease the basicity of the nitrogen atom as much as the 16-oxo group did in IIb and, consequently, the fragmentation of Πc is directed mainly by the azanitrogen atom.

2. 17a-azasteroids

The following 2-(4'-methyl-1'-piperazino)-17a-azaandrostanes have been examined:





The mass spectra of these compounds are shown in Fig. 3. The electron impact induced fragmentation of IIIa-c indicates that as the basicity of the 17a-aza-nitrogen atom decreases, its fragmentation-directing role will be surpassed by the other competing reaction centre, namely by the N-methyl-piperazino group.

The mass spectrum of IIIa shows a molecular ion of medium intensity, which readily loses a CH_3^{\cdot} group. Elimination of a water molecule involving β -cleavage to an amino-nitrogen atom occurs as a competing primary process. The loss of the N-methylpiperazine part and various cleavages of this group lead to abundant ions at m/z 70, 113 and to ion $(M-113)^+$. The great extent of the fragmentation for IIIa is due to the different active centres competing for charge localization.

In the case of **IIIb** the main fragmentation route is again the loss of a CH_3^{\cdot} group from the molecular ion, and the pathways directed by the piperazino part are surpassed, as compared to **IIIa**; *i.e.* a methyl substituent seems to enhance the charge localizing and fragmentation-directing effect of the aza-nitrogen atom.

In conclusion, the fragmentation of the 17-aza- and 17a-azasteroids examined is extremely selective, due to localization of the positive charge mainly on the nitrogen atom, and so the decomposition of the skeleton is surpassed. Decrease, however, of the basicity on the nitrogen atom and the presence of other charge localizing centres (either within the streoidal skeleton or as a substituent) result in the decomposition of other parts and the skeleton itself, consequently the mass spectrum will provide more information about the structure of the compound.

3. Steroidal alkaloids

The compounds investigated were the following:



Fig. 4 shows the mass spectrum of solasodanol (IVa), together with that of tigogenin (reported earlier [16]). The latter is a steroidal sapogenin of analogous structure having an oxygen atom in the F ring instead of an NH group. The mass spectrum of solasodanol (IVa) and that of its stereoisomer, tomatidine (Va), were found identical within the limits of reproducibility, *i.e.* the spectrum shown in Fig. 4 corresponds to both of them. The spectra in Fig.



4 indicate that the electron impact induced fragmentation of IVa and Va is much more selective than that of tigogenin. IVa and Va undergo decomposition via two fragmentation processes leading to ions at m/z 114 and 138, respectively. They arise via routes shown in the Figure and contain a positively charged nitrogen atom. The mechanism of their formation seems obviously to be the same as proposed by DJERASSI *et al.* [16] for the formation of ions at m/z 115 and 139 of the analogous tigogenin. No other fragmentation processes characteristic of the latter compound can be observed in cases of solasodanol and tomatidine, due to the presence of the NH group instead of the O atom.

The mass spectrum profoundly changed on acylation of the nitrogen atom, as it can be seen from the mass spectra of IVb-e and Vc, Ve (Figs 5-7). These spectra exhibited molecular ions and ions at m/z 114, 113 and 138 together with their acyl-substituted analogues: $(113 + R_2-H)^+$, $(114 + R_2-H)^+$ and $(138 + R_2-H)^+$, respectively; furthermore, there are fragments arising by cleavages of the steroidal skeleton. The fragmentation pathways were supported by metastable transitions and by on-line computerized high resolution technique for O,N-diacetylsolasodanol (IVc). The data obtained are summarized in Table I. In the cases of acylated derivatives numerous of the observed fragmentation processes were found to be analogous to those


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decribed by DJERASSI for tigogenin, and furthermore a series of ions seem to be common (c, e, f, g and h).







$$m = g - CH_3$$
$$n = m - HOR_1$$
$$o = g - OR_1$$
$$p = f - HOR_1$$

The acylated derivatives of IVa and Va favourably decompose by the loss of R_2 (and R_2 —H), leading to ion k.

The ion l arises by losing an X[•] radical from the molecular ions of compounds having an >N-CO-X group. In the case of O,N-diformylsolasodanol (IVb, X=H) this process is not significant, but it results in abundant ions, when X=CH₃ or C_2H_5 (IVc, Vc, IVd). As the elimination of X[•] from N-acylated cyclic amines generally is not a significant process, the formation of l ions cannot be explained as a simple homolytic bond rupture. It is reasonable to regard it as a two-step process, starting with a hidden ring opening reaction: Loss of a $C_5H_9^{\bullet}$ radical from the molecular ions is a common process also for



n/z (observed)	m/z (calc.)	Chemical formulae
499.3672	499.3662	$C_{31}H_{49}NO_4$
484.3402	484.3427	$C_{30}H_{46}NO_4$
457.3622	457.3537	$\mathrm{C}_{29}\mathrm{H}_{47}\mathrm{NO}_{3}$
456.3550	456.3478	$\mathrm{C_{29}H_{46}NO_{3}}$
430.2928	430.2958	$\mathrm{C}_{26}\mathrm{H}_{40}\mathrm{NO}_{4}$
399.2924	399.2900	$\mathbf{C_{26}H_{39}O_{3}}$
344.2690	344.2715	$\mathrm{C}_{23}\mathrm{H}_{36}\mathrm{O}_{2}$
329.2460	329.2480	$\mathrm{C}_{22}\mathrm{H}_{33}\mathrm{O}_{2}$
315.2319	315.2324	$\mathbf{C_{21}H_{31}O_2}$
285.2588	285.2583	$\mathbf{C_{21}H_{33}}$
269.2274	269.2270	$C_{20}H_{29}$
255.2127	255.2113	$\mathrm{C_{19}H_{27}}$
222.1492	222.1494	$\mathrm{C_{13}H_{20}NO_{2}}$
216.1872	216.1878	$C_{16}H_{24}$
180.1396	180.1388	$\rm C_{11}H_{18}NO$
161.1337	161.1331	$\mathrm{C_{12}H_{17}}$
156.1034	156.1025	$\rm C_8H_{14}NO_2$
155.0936	155.0946	$\rm C_8H_{13}NO_2$
138.1290	138.1283	$C_9H_{16}N$
122.1087	122.1095	C_9H_{14}
114.0923	114.0919	$C_6H_{12}NO$

Table I

High resolution mass spectrum of O,N-diacetylsolasodanol (IVc) (70 eV)

IVc, Vc, and IVd. The $C_5H_9^{\circ}$ radical comes most probably from the $C_{23}-C_{27}$ moiety of the skeleton (ring F). Besides the fragmentation processes analogous to those observed for IVa and Va, some interesting reactions specific to the given compound were found: e.g. the molecular ion, as well as ions f and m of IVd can lose either a propionic acid or a neutral propiolactone molecule (formation of M-74 and M-72 ions, respectively). It is interesting that the latter process is energetically favourable, as low electron energy (14 eV) measurements have shown it: e.g. [f-72]/[f-74] = 0.5 at 70 eV, and ~ 2 at 14 eV. Particularly interesting differences were observed in the mass spectrometric behaviour of the N-nitroso derivatives (IVe, Ve). Their mass spectra differ from those of the other acyl-substituted compounds not only in the relative abundances of ions arising in analogous pathways, but also in the appearance of some new interesting processes. For instance, the appearance of the ion M-44 is rather surprising. Exact mass measurement revealed that this ion arises by the loss of N₂O from the molecular ion. This surprising



Table II

Relative abundance of $(M-44)^+$ ions for some N-nitrosopiperidine derivatives*

process has not been described for cyclic N-nitrosamines. From a survey of the published mass spectra of numerous nitrosamines it has been established that the $(M-44)^+$ ion is significant only in the mass spectra of cyclic nitrosamines which have many substituents in the surroundings of the N-NO part of the molecule, or possess a cyclic structure of low stability (see compilation in Table II).

In conclusion, the significant abundance of $(M-N_2O)^+$ ions (i) is attributable to the sterically crowded and/or strained cyclic structure of **IV**e and **Ve**.

According to the metastable transitions, the $(M-N_2O)^+$ ions can lose a $C_2H_5^{\cdot}$ group, in which elimination of carbon atoms from the $C_{20}-C_{21}$ positions takes place.

Comparing the relative abundances of the fragment ions containing no nitrogen atom, produced from IVa, Va and their derivatives, interesting changes can be observed (see Table III). These data reveal that while for unsubstituted solasodanol and tomatidine practically all fragments contain N atom, the abundance of fragments without N atom becomes significant in cases of the acylated derivatives, indicating the large differences in the fragmentation-directing role of the nitrogen atom in these compounds.

In the cases of solasodanol and tomatidine the fragmentation starts with homolytic cleavage of the $C_{20}-C_{22}$ or the $C_{22}-O$ bond (both are in

^{*} Abundance data are taken from Ref. [18]

Compounds	$I/\Sigma I \% 100$
IVa	4
Va	4
IVb	36
IVc	24
Vc	20
IVd	25
IVe	64
Ve	62

Table III

Relative abundance of fragments containing no N atom, in the mass spectra of solasodanol, tomatidine and their derivatives*

* Abundance data are expressed in the percentage of the total ion current

 β -position to the nitrogen atom), leading to ions a, b, d and M-28. For the acyl-substituted compounds, however, the ruptures of the $C_{22}-N$ and/or $C_{22}-C_{23}$ bonds also occur as significant primary processes (formation of ions f, h, i, g). Consequently, the mass spectrometric behaviour of steroidal alkaloids also strongly depends on the basicity of the nitrogen atom (like in the aza- and amino-aza compounds). Decreasing its basicity, the directing role of the hetero atom in the fragmentation decreases, and new primary fragmentation processes arise, so the further decomposition of the ions resulting in this way will provide more structural information.

Table IV

Main types	I/Σ I (%)										
of ions	IVe	Ve									
M [m/z 444]	1.4	3.2									
M - NO [m/z 414]	9.1	11									
j [m/z 400]	8.9	11									
$j - \mathrm{C_2H_5} \; [m/z \; 371]$	7.3	8.2									
$h \ [m/z \ 357]$	16	16									
$f \ [m/z \ 273]$	12	13									
d [m/z 138]	8.1	6.4									
$b \ [m/z \ 114]$	10	7.4									

Major ions in the mass spectra of N-nitrososolasodanol (IVe) and N-nitrosotomatidine (Ve)

Comparison of the mass spectra of the IV and V stereoisomeric pairs made possible a study of the mass spectrometric effects of this steric difference, which had not been investigated so far.

As it has been mentioned, the mass spectra of compounds IVa and Va were found to be identical. In contrast the mass spectra of IVc-Vc and IVe-Ve differ in the abundances of certain fragments, *i.e.* these isomers are distinguishable on the basis of the mass spectra. Especially significant differences were observed in the case of N-nitroso derivatives (IVe-Ve). The differences for the stereoisomeric pairs seem to be due to the different molecular ion stabilities (see Table IV), and can be attributed to the differently crowded structures of the stereoisomers.

Experimental

The mass spectra were obtained with an AEI MS-902 mass spectrometer operating at 70 eV electron energy and 150 °C ion source temperature.

The exact mass measurements were carried out using an on-line computer technique (Instem DATAMASS-ONE), with an accuracy of ± 10 ppm of the calculated values.

The syntheses of the compounds Ia - c, IIa - c, 3β -hydroxy- 5α -androstane and IIIa - cwill be published elsewhere.

 \hat{S} olasodanol and tomatidine (IVa. Va) as well as their derivatives (IVb-c, Vc, e) were kindly furnished by Dr. L. TOLDY.

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THE MASS SPECTRA OF NITROGEN-CONTAINING STEROIDS, II*

8-AZAGONA-12-ONE AND D-homo-8-AZAGONA-12-ONE STEREOISOMERS

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As shown by a comparative study of some stereoisomeric pairs of the title compounds, there are interesting stereoselective fragmentation pathways of diagnostic value in elucidating stereochemical problems, occurring during the electron impact induced decomposition of these isomeric systems.

In the case of the C/D *cis/trans* isomeric pairs much easier loss of a $C_3H_7^+$ radical from ring D or of a C_4H_7O group from the C and D rings of the ionized molecule has been found for the C/D *cis* isomer, resulting in significant differences in the *e.i.* mass spectra. At the same time, in the case of B/C *cis/trans* isomers, which gave identical *e.i.* mass spectra, characteristic, stereoselective first field free region metastable processes $(M \rightarrow m/z \ 191$ and $191 \rightarrow 176$ transitions) have been observed by means of IKE spectroscopy.

Introduction

Effects of stereochemistry on the mass spectrometric fragmentation of streoids have been a subject of extensive study over the last two decades. First of all the mass spectra of *cis/trans* isomers in A/B ring junction have been compared (e.g. [2-4]) and were found to be diagnostically different, but studies on steroids of different B/C or C/D ring anellations have also been reported (e.g. [5-7]). As to nitrogen-containing steroids, only one paper (PANDIT *et al.* [8]) is known to us to deal with stereochemical effects on the mass spectra of azasteroids.

In the present work we report the results of our comparative mass spectrometric examination of the following stereoisomeric system of nitrogencontaining steroids:



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MÁK et al.: NITROGEN-CONTAINING STEROIDS, II

		Ι		II	
	n	= 3		n =	4
	9H	13H	14H		
Ia	α	x	x	B/C trans,	C/D cis
Ib	β	x	x	B/C cis,	C/D cis
IIa	x	β	x	B/C trans,	C/D trans
IIb	β	x	x	B/C cis,	C/D cis
IIc	β	β	x	B/C cis,	C/D trans

Ia and Ib, differing only in the B/C ring junction, correspond to a B/C *cistrans* isomeric pair, and the same is the case for IIa and IIc. However, IIb having C/D *cis* geometry, is dissimilar to both IIa and IIc; at the same time, IIb and IIc form a C/D *cis-trans* stereoisomeric pair.

Results and Discussion

Comparison of the mass spectra

The high resolution mass spectral data of Ia, b and IIa-c are summarized in Table I.

As the data show for the Ia and Ib isomers, the electron impact mass spectra of this B/C *cis/trans* isomeric pair are practically identical. The same applies to the IIa and IIc stereoisomers, *i.e.* difference in the B/C annellation has no effect on the abundance of the fragment ions. The mass spectrum of IIb, however, exhibited significant differences in the relative intensities of some fragment peaks, as compared with those of IIa or IIc. In the low resolution mass spectra of IIa, b, c such peaks were found to be first of all due to the $(M-43)^+$ fragments, but also to the peaks $(M-57)^+$, $(M-71)^+$ and $(M-85)^+$, all of them being more abundant for IIb, thus indicating the lower mass spectrometric stability of this isomer. As it turned out in the course of high resolution measurements, the $(M-43)^+$ and $(M-57)^+$ peaks appeared as doublets, *i.e.* both of them consist of two kinds of ions (see Table I).

The $(M-43)^+$ peaks are composed of $(M-C_2H_3O)^+$ and $(M-C_3H_7)^+$ ions. In accordance with the abundance values, the formation of the latter ion, namely the loss of $C_3H_7^-$ radical from the molecular ion, is a very stereoselective reaction, which is favoured in case of the C/D-cis isomer, while the reaction leading to $(M-C_2H_3O)^+$ ions practically is not affected by stereoisomerism. On the basis of the intensity data, the formation of $(M-71)^+$ ions is also a very stereoselective process. To rationalize these interesting observations it is assumed that the starting step of all these fragmentation processes

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			Compounds		
Ions	Ia (B/C-trans, C/D-cis)	Ib (B/C-cis, C/D-cis)	Па (B/C-trans, C/D-trans)	IIb (B/C-cis, C/D-cis)	He (B/C-cis, C/D-trans
		R	elative abundances		
M	65	66	67	85	68
M - 1 [M - H]	100	100	100	100	100
$M - 29 [M - C_2 H_5]$	7.7	5.7			
$M = 43 \left\{ \begin{bmatrix} M - C_2 H_3 O \end{bmatrix} \right\}$	11	13	25	21	24
$[M - C_3 H_7]$	2.0	2.0	1.0	22	5.0
$[M - C_3 H_5 O]$			0.5	1.5	0.6
M = 57					
$[M - C_4 H_9]$			0.4	1.5	0.5
$M - 71 [M - C_4 H_7 O]$			1.0	11	1.4
$M = 85 [M - C_5 H_9 O]$			2.0	6.0	2.0
m/z 192 [C ₁₁ H ₁₄ NO ₂]	11	12	14	17	12
m/z 191 [C ₁₁ H ₁₃ NO ₂]	21	22	35	44	34
m/z 190 [C ₁₁ H ₁₂ NO ₂]	25	32	19	28	17
m/z 176 [C ₁₀ H ₁₀ NO ₂]	6.0	7.0	9.0	11	8.0

Table T	Ta	bl	le	1	
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Electron impact (70 eV) mass spectra of the 8-azagonane isomers (I-II)

is a C-C bond fission β to the nitrogen atom and, furthermore, that for the processes found to be stereoselective, this is a cleavage of one of the bonds of the C₁₄ carbon atom at the C/D ring anellation (routes A and C in Scheme 1).

The lack of stereoselectivity for the loss of C_2H_3O from the molecular ion suggests the cleavage of the C_9-C_{11} bond as a primary reaction step (route *B* in Scheme 1).

These primary steps in fragmentation routes A to C are followed by other, presumably not stereoselective C-C bond cleavages, as well as hydrogen migrations.

It is remarkable that fragmentation pathways analogous to A and B have also been proposed for 9-aza-D-homo-gona-13(14)-en-6-one [9] on the basis of deuterium labeling.

Comparison of the IKE spectra

The ion kinetic energy (IKE) spectra of Ia, b as well as IIa-c have also been taken and compared. The main peaks observed by this mass spec-



Table II

	Ia	Ib	Па	ПР	IIe								
Metastable transitions	(B/C-trans, C/D-cis)	(B/C-cis, C/D-cis)	(B/C-trans, C/D-trans)	(B/C-cis, C/D-cis)	(B/C-cis, C/D-trans)								
	Relative abundances												
$M \rightarrow M{-}15$	30	25	10	23	18								
$M \rightarrow M - 29$	20	18	_	_	_								
$M \rightarrow M - 43$	37	33	18	54	25								
$M \rightarrow M - 57$			_	17	13								
$M \rightarrow M - 71$			_	23	_								
$M{-}43 \rightarrow m/z \ 191$	35	37	28	26	31								
$M \rightarrow m/z \ 191$	89	100	58	68	71								
$m/z \ 191 ightarrow m/z \ 176$	100	89	100	100	100								
$[M ightarrow m/z \ 191]$	0.90	11	0.59	0.69	0.71								
$[m/z \ 191 \rightarrow m/z \ 176]$	- 0.09	1.1	0.58	0.08	0.71								

Ion kinetic energy (IKE) spectra of the 8-azagonane stereoisomers (I-II)

trometric method for detecting metastables and the corresponding transitions are summarized in Table II.

The relative abundance data reveal that there are significant differences between the IKE spectra of C/D *cis* and *trans* isomers **IIb** and **IIa**, **c**, similarly to their normal mass spectra.

(The peaks, corresponding to the $M^+ \rightarrow (M-43)^+$, $M^+ \rightarrow (M-57)^+$ and $M^+ \rightarrow (M-71)^+$ metastable transitions are of greater abundance in case of **IIb** than for **IIa** and **IIc**, in accordance with the intensity data of the appropriate normal ions shown in Table I.)

It is of particular interest that the IKE spectra of the B/C *cis* and *trans* isomeric pairs have also been found to be distinguishable: significant and characteristic differences are observed in the relative intensities of peaks for the $M^+ \rightarrow m/z$ 191 and m/z 191 \rightarrow 176 transitions occurring in the first field free region of the double focussing mass spectrometer, either in the case of the Ia and Ib pair or the IIa and IIc isomers. The intensity ratios of these peaks are higher by 20 per cent for B/C *cis*, than for B/C *trans* isomers (*cf*. Table II). At the same time, this ratio seems to be independent of the geometry at the C/D ring junction, as it can be seen when comparing data for IIb and IIc. The fragmentation pathways leading to the formation of ions m/z 191 and 176 are shown in Scheme 2.



Scheme 2

Summing up the results of this comparative study, in the electron impact mass spectra of the C/D cis/trans stereoisomers examined, marked differences were obtained which were found to be mainly due to a much easier loss of a C₂H₇ radical from ring D or of a C₄H₂O group from the C and D rings of the molecular ion in case of the C/D cis isomer of the II series.

In case of the B/C cis and trans isomers, which gave identical EI mass spectra, interesting stereoselective (metastable) processes were observed by means of IKE spectroscopy for detecting the metastable decompositions of ions.

These observations concerning stereochemical effect on the mass spectrometric behaviour seem to be applicable for distinguishing stereoisomers of related compounds.

Experimental

All mass spectra were obtained with an AEI MS-902 mass spectrometer at an electron energy of 70 eV and 150 °C ion source temperature. IKE spectra were taken changing the ESA voltage at an accelerating potential of 8 kV.

The synthesis and characterization of the compounds examined have been described elsewhere [10].

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Ernő NEMECZ: Clay Minerals

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The thirties and forties of the present century witnessed the beginnings of the study of clay minerals, but its hey-days fall in the fifties and sixties, in parallel with the development of instrumentation in the relevant field, first of all in that of X-ray studies, then in thermal analysis, infrared spectroscopy, and electron microscopy. The basic properties of the clay minerals have been elucidated with the help of these instruments. This is the period also of the publication of comprehensive monographs. Among others, there appeared R. E. GRIM's "Clay Mineralogy" (1953), R. JASMUND's "Die Silikatischen Tonminerale" (1955), C. W. BRINDLEY's "Ray Identification and Crystal Structures of Clay Minerals" (1951, new ed. 1961), G. MILLOT's "Géologie des Argiles" (1964). These are decisively mineralogically oriented; the up-to-date book by MILLOT deals with the prominent role played by clay minerals in geological processes.

This handbook in English, by Ernő NEMECZ, is a translation of his "Agyagásványok" published by the Akadémiai Kiadó, in 1973, but contains some additional material. This volume is of 547 pages, with 217 illustrations, 126 Tables, Authors' Index and a Subject Index. It is divided into three parts, preceded by a preface, and an introduction by the author.

Part I, the longest, deals with the internal structures of clay minerals. Part II is about methods of determination or identification, and Part III about the genetics of clay minerals. The distribution according to volume is as follows: Part I, 258 pages, list of references 14 pages; Part II, 78 pages, list of references 2 pages; Part III, 143 pages, list of references 8 pages. The importance of the several parts is well characterized by these data. Limits imposed by the space available prevented the inclusion of subjects like the colloid chemistry of clay minerals, and discussion of their technological relevance, because to satisfy the great interest deriving from aspects of practical utilizations would have been impossible in this volume, writes the author. The Table of Contents reveals that the several parts are well arranged and easy to survey.

In Part I the fundamental general crystal structures of clay minerals are characterized. Detailed discussions are to be found on the deformation phenomena of the octahedral and tetrahedral layers in clay minerals, these may indirectly affect the magnitude of the *c*-period and of the (001)-reflexions which are correlated with it. These deformation phenomena may cause, moreover, the change, in function of chemical composition, of the magnitude of the *b*-period which is indirectly deducible from the (060)-reflexion in X-ray studies. Following a general characterization there is a good survey of the most important groups of the clay minerals (*cf.* Table 2).

The principal chapter of Part I is an exposition of the types of clay minerals based upon crystal structure, X-ray patterns and parameters. This chapter has been extended by the description of some clay minerals not dealt with in the Hungarian original, also some X-ray data, and bibliographical items have been added.

In part II, about the methods of examination, are to be found the many-sided techniques for the exact characterization of clay minerals. Thus, chemical analyses, recording of polarization, electron microscopic examinations, infrared spectra, X-ray diffraction patterns and thermal dilatometric data are discussed. Numerous illustrations, diagrams, and most revealing electron microscopic photographs considerably facilitate the identification of single species of clay minerals. Original Tables (cf. Tables 91...94) help to distinguish between types which produce similar basic reflections. Very useful are Tables 98 and 99 in the identification of different types of clay minerals with different basic reflexions and simultaneously present in the sample. The author is past master in X-ray analysis: the chapter can be said to be the most rounded off and most thoroughly interpreted part in this book.

Part III, the genetical part, has two chapters, of which the first deals with experimental studies of the genesis of clay minerals. Here the mechanism how primary minerals are transformed into clay minerals, and how structural fragments produced by the decomposition of primary minerals are synthesised into clay minerals, are discussed on the basis of a theoretical appraisal of the ample international literary material.

The second chapter deals with investigations of the natural processes which yield clay minerals in diverse geological formations, viz. within the 0 to 5 km belt of the continental crust, then upon the dry surface of the crust, finally within the hydrosphere. Hydrothermal generation of clay minerals in the 0 to 5 km belt is paid special attention and is described in detail. Here a number of results Hungarian obtained mainly in collaboration with GY. VARJU, are referred to. For the discussion of the beltwise correlation of ore formation and generation of clay minerals. In my opinion geologically better founded Hungarian examples could have been cited than those of Mátraszentimre.

As far as the hydrosphere is concerned, a summary — chiefly based on international results is given on sedimentation in lakes, rivers and oceans; but some Hungarian formations are mentioned. The sedimentational processes which yield clay minerals are summarized in the well-arranged Table 126.

All in all, it is great joy that we can greet this book by Professor NEMECZ. This is one of the few comprehensive Hungarian works on a geological topic that has been published in English and thus made accessible for non-Hungarian readers. It is a justified hope that the professional level and exposition offered in this book will earn recognition abroad of Hungarian scientific efforts. Also the good English translation and the beautiful presentation both contribute to the success of this book.

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H. DALLMAN und K.-H. ELSTER: Einführung in die höhere Mathematik für Naturwissenschaftler und Ingenieure, Band II

Fischer - Verlag Jena, 1981, 580 Seiten

Zur alltäglichen Arbeit der Physiker und Forschungsingenieure unserer Zeit ist die Kenntnis nahezu sämtlicher Zweige der modernen Mathematik unerlä {lich. Weit über den klassischen Lehrstoff der Differential- und Integralrechnung und der analytischen Geometrie hinaus benötigt der Naturforscher und Projektingenieur heute eine ziemlich gründliche Kenntnis der Differentialgleichungen, der Lehre der komplexen Funktionen, der Wahrscheinlichkeitsrechnung und der mathematischen Statistik, er kann aber auch Disziplinen wie die Funktionalanalyse, die mathematische Logik und die Distributionstheorie nicht entbehren. Selbstverständlich ist es unnötig, in diese Zweige so weitgehend wie der auf dem betreffenden Gebiet forschende Mathematiker einzudringen; über gut fundierte Kenntnisse soll jedoch jeder Naturforscher und Ingenieur verfügen, besonders was diejenigen betrifft, die auf seinem eigenen Arbeitsgebiet Anwendung finden. So ist z. B. die Funktionalanalyse für den Quantenphysiker, den Quantenchemiker und den in der Forschung tätigen Elektroingenieur unerläßlich. Um jedoch die mathematischen Zusammenhänge bezüglich der Banachschen und Hilbertschen Räume zu verstehen, sind bestimmte topologische und mengentheoretische Kenntnisse notwendig.

Auch ist eine wesentlich tiefere und breitere Kenntnis der linearen Algebra nötig, als früher in Vorlesungen über analytische Geometrie vermittelt wurde.

Es ist weiterhin selbstverständlich, daß sowohl der Naturforscher als auch der in der Forschung tätige Ingenieur über umfassende und aus – führliche Kenntnisse der Differentialund Integralrechnung von Funktionen mit mehreren Variablen verfügen muß.

In der mathematischen Fachliteratur erscheinen immer mehr Bücher, die diesen Ansprüchen zu entsprechen versuchen. Sie streben eine klare und bündige Darstellung der einzelnen Fachgebiete der Mathematik an und heben die entsprechenden Anwendungsmöglichkeiten hervor, d.h. es wird gezeigt, wo und wie diese Zweige der Mathematik in der Physik und den technischen Wissenschaften angewendet werden können und sollen. Ziel ist also nicht die theoretische Analyse der mathemtaischen Sätze und Kusammenhänge, sondern eine möglichst klare und verständliche Darstellung der modernen Mathematik als unerläßliches Werkzeug für den Naturforscher und Ingenieur.

Dieses Ziel haben sich auch die Professoren H. DALLMANN und K.-H. ELSTER gesetzt. Der erste Band ihres Werkes erschien bereits vor mehreren Jahren und wurde von uns ausführlich rezensiert. Der jetzt erschienen II. Band ist das Ergebnis einer sehr gründlichen und umfassenden Arbeit. Er ist in fünf Kapitel gegliedert, namentlich

I. Grundbegriffe der Analysis und Topologie;

- II. Lineare Algebra;
- III. Funktionen von mehreren Veränderlichen;
- IV. Differentialrechnung für Funktionen von mehreren Veränderlichen;
- V. Integralrechnung für Funktionen von mehreren Veränderlichen ..

Diese Kapitel sind in insgesamt 28 Abschnitte unterteilt.

Kapitel I (Umfang 105 Seiten) besteht aus folgenden Abschnitten:

1. Mengentheoretische Hilfsmittel

Der Abschnitt besteht aus sechs Teilen und befaßt sich mit den Operationen mit abstrakten Mengen und Mengensystemen, die durch viele Abbildungen veranschaulicht werden. Auf das direkte Produkt von Mengen und auf den oberen und unteren Limes von Mengen folgen wird einegangen und auch der Begriff Algebra und auch der Begriff Algebra und Sigma-Algebra erwähnt.

2. Relationen und Abbildungen

Der Begriff der Relation und die Operationen mit Relationen werden im Buch gedräng t und kurz behandelt, um darauf besierend den Begriff der Abbildung (Funktion) einführen zu können. Diese Teile sind — infolge der Kürze und Abstraktheitkein leichter Lesestoff, obwohl die Verfasser auch danach streben, die abstrakten Begriffe und Zusammenhänge durch anschauliche Bilder verständlich zu machen. Es wereden die Zermelolschen Auswahlaxiome, der Satz der wohlgeordneten Mengen und im Zusammenhang mit den halbgeordneten Mengen das Zornsche Lemma erwähnt und die Sätze der Boole-Algebra und ihre Anwendung bei elektrischen Leitungen, die sog. Schaltalgebra zusammengefaßt. Letztere wird durch mehrere konkrete Beispiele und Abbildungen anschauluch gemacht.

Dieser Abschnitt benötigt unbedingt eine orale Erklärung durch den Professor, weil der Stoff für Physik- und Ingenieurstudenten der niederen Semestern zu schwer ist.

3. Topologische Räume

Dieser Abschnitt (Umfang 25 Seiten) behandelt die wichtigsten Grundsätze der sog. mengentheoretischen oder allgemeinen Topologie. Es wird nur soviel mitgeteilt, als zum Verständnis der folgenden Abschnitte über die metrischen, Banachschen und Hilbertschen Räume unbedingt notwendig ist. In diesem Abschnitt werden auch die kontinuierlichen Abbildungen (Funktionen behandelt. Einige Seiten sind den linearen topologischen Räumen gewidmet.

4. Metrische Räume

Dieser Abschnitt (14 Seiten) faßt die Elementarbegriffe der metrischen Räume zusammen: Konvergenz der Punktfolgen, Cauchy-Folgen, Begriff des vollständigen metrischen Raumes und separable Räume sind jene Teile, die die Grundlage zum Studium der normierten Vektorräume, der Banachschen und Hilbertschen Räume darstellen, deren Kenntnis wiederum für das Verständnis der Funktionalanalyse unerläßlich sind. Mit der Funktionalanalyse befaßt sicht eigentlich kein Abschnitt gesondert, doch vermittelt der folgende Abschnitt 5: Normierte Vektorräume, Banachsche und Hilbertsche Räume, im wesentlichen die Vorkenntnisse zum Studium der Funktionalanalyse.

Kapitel I schließt mit dem Abschnitt 6, worin die \mathbb{R}^n -Räume der "n" reellen Zehlen und die \mathbb{K}^n -Räume der "n" komplexen Zahlen auf einigen Seiten gesondert behandelt werden. Der siehen Seiten umfassende Teil über die konvexen Mengen des \mathbb{R}^n -Raumes ist eine Vorbereitung zur linearen Programmierung, obwohl von Programmierung in diesem Teil nicht die Rede ist. Dieser Teil über die konvexen Mengen ist sehr gedrängt gefaßt und erfordert deshalb eine erhebliche Mitarbeit des Lesers.

In Kapitel II wird auf 124 Seiten die lineare Algebra ziemlich ausführlich behandelt. In den Abschnitten 7 und 8 werden zunächst Vektorräume eingehend erläutert. Die Schlüssel-

worte dieses einleitenden Teils sind: Basis des Vektorraums, lineare Unabhängigkeit und Abhängigkeit, Unterräume, lineare Mannigfaltigkeiten, Faktorräume. Es folgen die Behandlung von linearen Funktionalen, die linearen Abbildungen von Vektorräumen in andere Vektorräume (speziell lineare Abbildungen $R^l \to R^m$) und kurzgefaßt der Begriff des linearen Operators.

Abschnitt 9 (34 Seiten) befaßt sich mit der Matrixrechnung. Schon der Begriff der Matrix wird anhand mechanischer und elektrotechnischer Beispiele erläutert; auch im weiteren ist der theoretische Teil eng mit den Anwendungen verbunden. Die Theorie der in der Elektrizitätslehre äußerst wichtigen linearen Quadrupole wird ausführlich behandelt; ein gesonderter Teil zeigt die Anwendung der Matrixrechnung in der Betriebswirtschaft. Die beigefügten zahlreichen Aufgaben erleichtern das Erlernen der Matrixrechnung.

Abschnitt 10 befaßt sich mit der Lösung von linearen Gleichungssystemen und mit der Struktur der Lösungen, wobei der in der Praxis so wichtige Gauss-sche Algorhythmus eingehend behandelt wird. Die Bezeichnungen entsprechen der modernen Vektor-Schreibart.

Abschnitt 11 behandelt die Eigenschaften der Determinanten in engem Zusammenhang mit den Vektorräumen. Es wird gezeigt, wie Determinanten den Elementen ihrer Reihen oder Säulen nach entwickelt werden. Auch die Laplace'sche Entwicklung wird dargelegt, jedoch ohne Beweis. Der Begriff des Rangs der Matrix wird mit Hilfe der Determinanten erläutert und die Cremer-Regel der Lösung linerarer Gleichungssysteme angeführt. Abschließend wird die Anwendung der Determinanten zur Berechnung von inversen Matrizen gezeigt.

Abschnitt 12 befaßt sich mit dem Eigenwert-Problem, im wesentlichen nur für den Fall van quadratischen, symmetrischen, reellen Matrizen. Reelle, aber asymmetrische Matrizen werden nur kurz berührt.

Im 13. Abschnitt wird eine kurze Zusammenfassung der Theorie der bilinearen und quadratischen Formen mit der geometrischen Deutung der quadratischen Formen vorgelegt. Des Kapitel über lineare Algebra schließt mit den Gram-Determinanten ab.

Kapitel III behandelt auf 33 Seiten die Eigenschaften der reelen Funktionen von mehreren Veränderlichen, namentlich der Funktionen $\mathbb{R}^n \to \mathbb{R}$, $\mathbb{R} \to \mathbb{R}^n$ und $\mathbb{R}^n \to \mathbb{R}^m$. Auch die Anwendung von räumlichen Zylinder- und Polarkoordinaten wird ausführlich behandelt. Beim Grenzwert der Funktionen von mehreren Veränderlichen wird auch auf den iterierten Grenzwert sowie auf den Begriff des relativen Greznzwerts der auf irgendeine Teilmenge des Definitions bereichs beschränkten Funktion eingegangen. Neben der Kontinuität wird auch der Begriff der Halbkontinuität erwähnt. Für den Leser, der Interesse an der mathematischen Programmierung hat, ist der 7 Seiten umfassende Teil des Buchs über konvexe Funktionen von mehreren Veränderlichen sehr nützlich.

Auf dieses vorbereitende Kapitel ist das nächste Kapitel aufgebaut: Kapitel IV; Differentialrechnung für Funktionen von mehreren Veränderlichen (Umfang 126 Seiten).

Nach einer Einführung in die partiellen Derivierten wird der Begriff der differenzilerbaren Funktion erläutert und anschließend der des totalen Differentials, alldies in moderner wektorialer Behandlungsweise. Der Zielsetzung entsprechend behandelt das Buch eingehend die Anwendungen des totalen Differentials in der Geometrie, in der Fehlerrechnung und in der Thermodynamik. Dieser letztgenannte Teil soll wegen seines großen Interesse für Naturforscher besonders hervogehoben werden. Hier werden noch die Derivierte nach Richtung, der Gradient skalarer Funktionen, die Differenzierbarkeit konvexer Funktionen und die Differenzierung von Determinanten behandelt, und zwar ebenfalls in moderner Weise mit den Bezeichnungen der Vektorrechnung, wodurch eine gedrängte Darstellung allgemeinen Charakters ermöglicht wird.

Im Abschnitt 19 werden der Mittelwertsatz der Funktionen von mehreren Veränderichen und die Taylor-Formel abgehandelt.

Abschnitt 20 ist sehr interessant: darin werden die impliziten Funktionen, deren Kenntnis — unter anderem — für die Theorie der Differentialgleichungen sehr wichtig ist, behandelt. Die eine zentrale Stellung einnehmende Jacobi'sche Matrix bzw. Determinante und die inversen Abbildungen, darunter die Transformation von rechtwinkligen Koordinaten in planare Polarkoordinaten sowie räumliche zylindrische und sphärische Koordinaten werden darin behandelt. Der Begriff der Abhängigkeit bzw. Unabhängigkeit von reellen Funktionen wird eingeführt. Dieses Thema ist in manchen Lehrbüchern der Analysis etwas vernachlässigt. da nur die lineare Unabhängigkeit bzw. Abhängigkeit erläutert wird. Der allgemeinere Begriff der Unabhängigkeit (Abhängigkeit), worin die Jacobi'sche Determinante die Hauptrolle spielt, ist jedoch für alljene unerläßlich, die sich eingehender mit der Theorie der Differentialgleichungen befassen wollen.

Abschnitt 21 hehandelt die freien und an Nebenbedingun en gebundenen Extremwertprobleme von Funktionen. Ein reichliches Material an Beispielen aus der Praxis, vor allem aus der Elekrotechnik macht den Text interessanter und wertvoller. Unter den Beispielen findet sich auch die hochwichtige Ausgleichsrechnung und Fehlerrechnung (zumindest ihre Grundlagen). Die zahlreichen und klaren Abbildungen erleichtern das Verständnis der Ausführungen.

Der Schlußabschnitt 22 des Kapitels IV befaßt sich mit den Differentialoperatoren der Vektoranalyse. Skalare und vektoriale Räume, statische und zeitlich veränderliche Räume, äquipotentiale Flächen von Skalarräumen werden kurz behandelt. Der Begriff der "Fendlinien" zur Veranschaulichung von Vektorräumen wird genau definiert. Danach folgt die Behandlung der Gradienten der Skalarräume mit den betreffenden Rechenregeln. Unter den Beispielen findet man auch den wohlbekannten Energiesatz der konservativen Kraftfelder. Im weiteren wird der Nabla-Operator als sympolischer Vektor eingeführt. Es folgt die Behandlung der Divergenz von Vektorräumen in höchst anschaulicher Form, so daß der Leser den Quellendichte-Charakter der Divergenz leicht begreifen wird. Auch hier wird der Text durch die Abbildungen gut ergänzt. Ein tieferes Verständnis des Divergenzbegriffs wird durch die Kontinuitätsgleichung und die Divergenz-Rechenregeln erzielt. Die Invarianz der Divergenz gegenüber orthogonaler Koordinatentransformationen wird gezeigt. Auch die Rotation von Vektorräumen ist, nicht zuletzt auch durch zahlreiche Abbildungen, sehr anschaulich dargestellt, wobei gezeigt wird, daß der Rotationsvektor bei Flüssigkeitsströmungen die Wirbeldichte des die Strömung beschreibenden Vektorraums kennzeichnet. Unter den Beispielen findet man die Rotation eines steifen Körpers um eine gegebene Achse, wobei gezeigt wird, daß die Winkelgeschwindigkeit (abgesehen von einem Faktor von 1/2) gleicht der Rotation der Umdreihungsgeschwindigkeit ist. Unter den Beispielen fefinden sich auch zwei Maxwellgleichungen, die jedoch nur berührt werden. Es folgen mehrfache Anwendungen des Nabla-Operators und schließlich die Verwendung von gekrümmten Koordinaten und die Darstellung der bisherigen Ergebnisse der Vektoranalyse mit Hilfe von gekrümmten Koordinaten.

Kapitel V behandelt die Integralrechnung mit Funktionen von mehreren Veränderlichen (145 Seiten). Der reiche Inhalt dieses Kapitels wird durch die Titel der Abschnitte angedeutet: Parameterintegrale; Kurvenintegrale; Ebene Bereichsintegrale; Räumliche Bereichsintegrale; Oberflächenintegrale; Integrälsätze der Vektoranalysis. Diese Abschnitte sind in weitere Teile gegliedert. Um einen Überblick über die Behandlung dieses äußerst wichtigen Teils der mathematischen Analyse zu egben, seine einige dieser Teile genannt: die Eulersche Gamma-Funktion; Potentialberechnung bei Potentialfeldern; Linienintegrale in der Thermodynamik; Transformation von planaren und räumlichen Integralen in neue Koordinaten; die Integralsätze von Gauss, Stokes und Green; vor den Doppelintegralen im planaren Bereich werden die nach Riemann (bzw. Jordon) meßbaren Mengen kurz erklärt. Hier werden keine Beweise geführt und es erfolgt keine tiefgehende Behandlung der Mengen. Bei den weiteren Ausführungen verbleiben die Autoren bei den nach Riemenn meßbaren Punktmengen, da diese für die Integralarten zu verstehen sind. Selbstverständlich bleibt demgemäß der Integralbegriff innerhalb des Reimann'schen Rahmens und Lebesgueintegrale werden nicht erwähnt.

Der vorliegende Band II des Lehrbuches erfüllt im gleichen Sinn wie Band I eine wichtige Aufgabe: all die Kenntnisse jenen Naturwissenschaftlern und Ingenieuren zu vermitteln, die höhere Mathematik zu ihrer Arbeit benötigen. Im Besitz dieser Kenntnisse können sie sich ungehindert mit allen Problemen der modernen Physik, Chemie und Ingenieurwissene schaften befassen. Da dafür notwendige mathematische Apparat steht in diesem Buch zur Verfügung. Zwar gibt es in der deutschsprachigen mathematischen Fachliteratur viele ausgezeichnete Bücher, die mannigfaltige Ansprüche sowohl der theoretischen Mathematiker als auch der an der Anwendung interessierten Physiker und Ingenieure befriedigen, jedoch befassen sich diese Bücher größtenteils mit nur je einem speziellen Gebiet der Mathematik, meostens auch eingehender und in größerem Umfang, als das vorliegende Buch; sie sind eher für den theoretischen Mathematiker als für den Naturforscher bzw. Ingenieur bestimmt. In den drei Bänden diese Lehrbuchs wird all das in modernen Auffassun, g Gehandlungsart und Bezeichnung zusammengefaßt, was ein forschender Ingenieur oder Physiker an mathematischen Kenntnissen benötigt. Ist er im Laufe seiner Forschungsarbeit dazu genötigt, auch andere Gebiete der Mathematik zu betreten, so kann er ruhig zu Spezialmonographien greifen, die er mit den durch das vorliegende Buch erworbenen Kenntnissen ohne Schwierigkeiten verstehen wird.

Ich bin davon überzeugt, daß der zweite Band des Lehrbuchs ebenfalls allgemeinen Beifall finden wird, vor allem bei dem Lehrpersonal und den Studenten der technischen Universitäten.

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D. KRÁLIK

Mössbauer spectroscopy, II The Exotic Side of the Method

Ed Uli GONSER, Volume 25 of the series "Topics in Current Physics"

Springer Verlag, Berlin 1981

This book (196 pp., 67 Figures) consists of nine chapters written by R. L. COHEN, H. FISCHER, V. I. GOLDANSKII, U. GONSER, S. S. HANNA, W. HOPPE, R. N. KUZMIN, R. L. MÖSSBAUER, V. A. NAMIOT, B. D. SAWICKA and J. A. SAWICKI.

The first volume of this book is Vol. 5 of the series "Topics in Applied Physics", published by Springer Verlag, Berlin, 1975, reviewed in Acta Chim. Acad. Sci. Hung., 89, 183 (1976). Chapter 1 ("Introduction"), 3 pp., 1 figure) was written by U. GONSER, the editor of

Chapter 1 ("Introduction"), 3 pp., 1 figure) was written by U. GONSER, the editor of the book. He gives information on the aim of publishing this second, new volume, which is to demonstrate some "exotic" possibilities of the application of Mössbauer spectroscopy when, instead of the common measurement techniques, less frequently applied measuring equipment is used, or when the subject of study is less common.

Chapter 2 "A Solution of the Phase Problem in the Structure Determination of Biological Macromolecules" (26 pp., 12 Figures) is by R. L. MÖSSBAUER, F. PARAK and W. HOPPE. One of the difficult problems in diffractional structure examination of biological macromolecules is phase determination. For phase determination, the authors make use of gamma-ray nuclear resonance scattering occurring on ⁵⁷Fe nuclei as reference nuclides. The technical difficulty of this work lies in the fact that it needs radiation sources of great activity (10⁹ Bq) in a small area $(2-4 \text{ mm}^2)$ and special detectors of high counting rate. The authors illustrate the applicability and, at the same time, its difficulties by demonstrating their measurements on a myoglobin single crystal.

Chapter 3 is "The Gravitational Red-Schift" (18 pp, 3 figures), written by R. V. POUND. It is well-known that among the measurement techniques existing in our times it is the Möss-BAUER effect that enables us to measure the smallest energy change. By this method changes of 10^{-10} eV occurring in the energy state of the nucleus can be measured. Applying MössBAUER spectroscopy, this permits to demonstrate the effect predicted by EINSTEIN in 1907, namely, that gravitation influences the frequency of electromagnetic radiation. The author demonstrates experiments in which the MössBAUER effect was used to prove the so-called gravitational red-shift, and he deals in detail with the experiments carried out in a tower built in 1884 for the Jefferson Physical Laboratory of the Harvard University.

Chapter 4 of the book (Trends in the Development of the Gamma Laser, 22 pp.) was written by Soviet authors: V. I. GOLDANSKII, R. N. KUZMIN and V. A. NAMIOT. They review the possible applications of gamma lasers and examine the new possibilities arising for Mössbauer spectroscopy if nuclei could be excited by gamma lasers. Though this topic is rather the futurology of the field than its present, it is an exciting thing, nevertheless, to think over, together with the authors, those interesting experiments which could be carried out if the technical conditions were developed enough to produce gamma lasers that are suitable for exciting nuclei producing Mössbauer effect. One of the possibilities dealt with by the authors is the transformation of nuclei, the mass number of which is less by one than that of the Mössbauer isotope, into excited nuclei with the necessary mass number, by pulsed neutronflux: $\frac{A}{Z} X + n \rightarrow \frac{A+1}{Z} X^*$. Nevertheless, the production of the necessary neutron generators

and the development of rapid methods for isotope separation are difficult technical tasks.

Chapter 5 (Nuclear Resonance Experiments Using Synchrotron Sources, 18 pp., 7 Figures) written by R. L. COHEN gives an overview of possible nuclear resonance experiments using synchrotron sources. The experiments proposed here are divided into two classes: nuclear fluorescence (or absorption) and nuclear Bragg scattering experiments. It is emphasized that for both categories the main technical difficulty arises from the fact that, among the photons of the synchrotron radiation, there are 10^8 times more candidates for electronic scattering, *etc.*, processes than for nuclear resonance, even if the bandwidth of the filtered beam is as narrow as 1 eV. Several propositions are discussed which would allow the experimentalist to overcome these problems.

Chapter 6 carries the title "Resonance γ -Ray Polarimetry" (40 pp. 19 Figures) by U. GONSER and H. FISCHER. After a brief introduction, a thorough mathematical description of the polarization phenomena is given in terms of density matrices. Then the general formalism is applied to the special case of hyperfine interactions in ⁵⁷Fe. Practical problems, such as the

production of polarized γ -radiations some applications to amorphous materials, as well as the observation of the Mössbauer-FARADAY effect are also discussed.

In Chapter 7 (Iron-Ion Implantation Studied by Conversion-Electron Mössbauer Spectroscopy, 28 pp., 19 Figures) V. D. SAWICKA and J. A. SAWICKA discuss the applications of conversion-electron Mössbauer spectroscopy in iron-ion implantation studies. The extremely high sensitivity of the method allows the study of ⁵⁷Fe doses lower than 10¹⁴ atoms/cm³. Beside reviewing the results achieved in this field so far, the authors pay great attention to the experimental techniques.

The title of Chapter 8 is "Selected 'Exotic' Applications" (18 pp.) by R. S. PRESTON and U. GONSER. The longest part of the chapter gives information on Mössbauer experiments in connection with relativity theory. Since the same problem is discussed in Chapter 3, in our opinion it would have been more practical to unite Chapters 3 and 8.

In Subchapter 8.2, the authors demonstrate the way of using the Mössbauer method for detecting small motions of macroscopic objects. An interesting experiment is the one carried out by Bonchev and his colleagues: they observed the breathing and flickering motions of the abdomens of ants with the aid of MÖSSBAUER spectroscopy. An absorber containing ¹¹⁹Sn was spread on the ants, and the motions resulted in a line broadening.

Subchapter 8.3 demonstrates applications concerning the modulation possibilities of gamma photons. One of the frequently used principles is the correlation between line broadening and diffusion to which attention has been called first by SINGWI and SJÖLANDER.

Subchapter 8.4, 8.5 and 9.6 deal with MÖSSBAUER spectroscopic experiments on iron oxide in aerosols, on archeological findings and on biological materials, respectively.

In this chapter, MÖSSBAUER spectroscopic studies on frozen solutions should also have been mentioned, since important information on solution chemistry can be obtained by such measurements.

Chapter 9 "The Discovery of the Magnetic Hyperfine Interaction in the Mössbauer Effect of ⁵⁷Fe" (6 pp., 2 Figures) by S. S. HANNA, is a personal account of the first few years of Mössbauer spectroscopy in a very vivid and fascinating style.

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A. VÉRTES and S. NAGY

Diffraction Studies on Non-Crystalline Substances

Edited by István HARGITTAI and J. W. ORVILLE-THOMAS

Akadémiai Kiadó, Budapest and Elsevier Scientific Publishing Company, Amsterdam 1981. pp. 894

The scientific activities started at the 11th International Congress of Crystallography (Warsaw, 1978) continued in numerous special fields among others in an International School organized under the title given above by the Diffraction Group of the Eötvös Loránd Physical Society at Pécs, Hungary. The invited lectures set the tone of the school and were followed by lively round-table discussions and short oral papers. The apparent success of the school prompted the Editors to invite many distinguished participants to survey in the form of a book the wide range of structural studies on non-crystalline materials which have been discussed during the meeting. This invitation by and the editorial work of HARGITTAI and ORVILLE-THOMAS resulted in a collection of twenty comprehensive "quasi monographic" accounts of various topics on the structures: of (a) gas molecules (b) liquids, (c) transition systems between non-crystalline and ordered materials, and (d) amorphous solids (films, alloys, etc.). Only N. KASAI's contribution fails to accomplish this standard.

Part One is devoted to studies on molecular structures in gaseous state by means of electron diffraction (e.d.) and theoretical calculations (e.g. the determination of harmonic potential functions). The theory and implementation of e.d. on gaseous materials and its impact on the study of molecular structures (e.g. internal rotation in molecules) are given by J. KARLE in two papers. K. KUCHITSU deals with the analysis of the geometrical parameters of free molecules while L. V. VILKOV presents a survey of the stereochemical features of various organic and organometallic molecules. The paper of A. H. LOWREY attempts to elucidate the complex problem of large amplitude motions in molecular systems by the use of various

techniques of spectroscopy (vibrational, microwave spectroscopy, magnetic resonance, etc.) combined with e.d. Thus it forms a linkage with the other two states (liquid and solid) of the substances.

Part Two helps to glimpse into the structures of liquids. The properties of molecular liquids are presented by M. D. ZEIDLER, while the ion-solvent, solvent-solvent and ion-ion interactions revealed by combined X-ray and electron diffraction techniques in aqueous electrolyte solutions are discussed by G. PÁLINKÁS and E. KÁLMÁN. A more esoteric approach to the liquid structures is given by K. HEINZINGER who demonstrates the power of the molecular dynamics method in these systems.

Part Three is introduced by the paper of A. GUINIER who aims to shed light on the continuously varying states of materials between the real crystals and disordered systems, viz. gaseous, liquid and amorphous. Starting from the dynamic disorder in crystals, he guides the readers through the mesophases to the liquids and amorphous solids. The polymorphism of the latter is classified by J. L. FINNEY in terms of various computer constructed models. The next paper deals with the phenomenon of paracrystallinity (R. HOSEMANN and B. STEFFEN).

Part Four presents examples of the applications of diffraction methods in the study of polymers (e.g. manifold investigation of elastomer-plastomer blends, particle dimension distribution, etc.). It is worth noting the meticulous calculations of conformational energy maps on atactic poly(methyl methacrylate), which are given by R. LOWELL and A. H. WINDLE. Studies of relevance to amorphous substances (films, metallic alloys) are reported in Part Five. Among others, G. S. CARGILL III. surveys the structural models which enable one to describe the structures of amorphous metallic alloys, while T. MIZOGUCHI provides the theory and experimental techniques of neutron diffraction applied in studying such amorphous alloys.

In accord with the title of the book, the experimental technique applied is overwhelmingly based on the diffraction of electrons, neutrons and X-rays encountering non-crystalline substances. Nevertheless, the authors also frequently rely upon the results of other methods as the various ways of spectroscopy, quantum mechanics, theoretical chemistry, etc., giving a broad approach to the subject surveyed. The reviewer as a crystallographer has found many contributions useful and stimulating in his own research especially in forming a generalized view of the complexity of crystalline and non-crystalline materials. Consequently, he is pleased to recommend this book to all researchers working either inside or outside the realm of diffraction studies covering both crystalline and non-crystalline materials.

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A. KÁLMÁN

Soviet Scientific Reviews, Section B, Chemistry Reviews, Vol. 3

Harwood Academic Publishers GmbH 1981

This is a new volume of the Chemistry Reviews series, which summarizes results of research in chemistry in the Soviet Union. The volume under review comprises four surveys, each of a little known domain of chemical science.

The first paper deals with "Investigations in the Field of Technetium Chemistry", its authors are V. J. SPITSYN, A. F. KUZINA, G. N. PIROGOVA, and O. A. BALAKHOVSKIJ. We are given a thorough summary of technetium chemistry, this summary considers the complete body of work done up to now on the investigation of this very rare metal.

A short historical survey precedes a discussion of the chemical properties of technetium. Its electron structure resembles that of manganese though there is some difference in the outer electron shells. Thus also chemical and physicochemical characteristic of the two element⁸ are similar. The various ionization potentials, redoxpotentials, complex formation, and spectroscopic features of technetium are dealt with, finally the preparation, production of the metal are described. These matters occupy 73 pages, and 152 references are given.

Also the next is an interesting subject especially for inorganic chemists, reviewed by A. M. SLADKOV, and entitle d "Carbyne, a New Allotropic Form of Carbon". Diamond, graphite and carbyne that forms chains and are known since twenty years are the three forms of carbon which show different ty pes of hybridization, consequently differ in crystal structure and physicochemical character. The various methods of the preparation of carbyne are discussed in detail: these methods chiefly use acetylene, respectively carbon as their starting mate-

rials. Less is told about physical properties and still less about the chemical characteristics of carbyne. This article takes 35 pages and 66 references are listed.

V. J. SPSTSIN, L. P. KAZANSKIJ, E. A. TORCHENKOVA: "Current Structural and Spectroscopic Investigations of Heteropoly-Compounds." The subject matter is the chemistry of iso- and hetero-poly compounds; the interpretation and critical survey of structural studies. A general characterization of the properties of the several compounds is given, and very useful Tables are presented in this context: it is a pity that these Tables are not extended to include every method of investigation. The chief source of what is told in this paper is the work done by the authors. Reference to the literature is given according to the importance of the papers in fact quoted, completeness in this respect has not been aimed at. The several hetero-polyanions are treated systematically; a great advantage of their classification here is that divergent properties of compounds with similar structures are easily compared.

The only organical chemical paper is the work of M. J. KABATCHNIK, N. N. BUBNOV, A. J. PROKOFJEV, and S P. SOLODNIKOV, entitled "The Tautomerism of Free Radicals. "Wandering' Valence". In order to be able to interpret the mechanism of a great number of chemical reactions the knowledge of the radicals formed in the course of these reactions is decisively important. Results of NMR and EPR studies furnish the primary foundation of this essay. The migration of hydrogen, hydrogenotropy, is discussed, so are the metallotropy in radicals which contain metals of the II and III groups, and the "elementotropy" in groups IV and V. The very detailed and informative text of nearly 100 pages, with 67 references, merits the attention of theoretical organic chemists and of NMR and EPR spectroscopists.

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J. NAGY

Andreas MAEHLY and Lars STRÖMBERG: Chemical criminalistics

70 Figures, 65 Tables, 322 Pages Springer Verlag; Berlin, Heidelberg, New York 1981

Its title reveals that this book is about the diverse chemical aspects of criminalistic work. It is composed of three principal parts, viz. Part A, General Introduction; Part B, dealing with the State of the Art; and Part C, Auxiliary Activities.

Preceded by a short historical survey, the notion of "Forensic Science" is explained in Part A; here also the place of chemistry within the set of relevant sciences is determined.

Part B is, perhaps, the most valuable one in this book: it is a compendious presentation most useful for those active in this field. Part B is divided into 13 chapters, some of which are subdivided again. These chapters are

I. Narcotics and Dangerous Drugs

II. Explosives

III. Polymers

IV. Fibres

V. Paints, Varnishes and Lacquers

VI. Glass

VII. Soil

VIII. Firearm Discharge Residues

IX. Fire Investigation

X. Questioned Documents

XI. Toxic Substances in Foods

- XII. Restoration of Erased Markings
- XIII. Miscellaneous

It is to be seen that the task of a chemist engaged in criminalistic work will embrace the very wide field that extends from narcotics, proceeds over explosives, paints, toxic substances, to the reconstruction of erased markings. In the several chapters, authors discuss the chemical possibilities of detection and identification; in the course of such a discussion the application of the most sophisticated and up-to-date instruments, and the complex utilization of a combination of such instrument are explained. A good example of this is the methodology concerning narcotics: here ultraviolet-, infrared-, and mass-spectrometers and various chro-

. . .

13*

matographic techniques are resorted to. The descriptions, severally, of some most important methods; of the means of identification of the various substances; of the commercially available chemicals are very important topics in this Part. Quite concisely, some basic knowledge indispensable for the understanding of these matters is conveyed in several of these chapters, a good example of this is the chapter about polymers. Generally, a practical example is given in each chapter: these examples serve to demonstrate the important role played by, and the great possibilities inherent in, chemical techniques utilized also in crime-detection.

We do not doubt, however, that the greatest service this book does offer to the workers in this field resides in the lists, at the end of the chapters, of references to the relevant literature mostly of the last decade.

The division of these bibliographies is very interesting and useful. General References lead to works which offer a general view of a given domain. Then we are given Methodology References, finally, Specific References: these go deepest in details either regarded from the point of view of methods or of substances to be determined.

In Part C the authors deal, first of all, with questions of organization, flow of information, and co-ordination of efforts.

To sum up: chemists, no matter whether beginners, or experts of some years' standing, in this field hold an important book in their hand. The beginner is offered an overall view of "Forensic Chemistry" that reveals its internal connexions, possibilities, and limits. The expert, on the other hand, is helped enormously towards completion of his knowledge by reference to the literature about the latest methods.

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L. HAZAI

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RESEARCH GOALS OF THE LABORATORY OF MACROMOLECULAR CHEMISTRY AND ORGANIC CATALYSIS*

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Two main research lines are developed in our laboratory:

- a first group is centered on polymer chemistry with particular emphasis laid on stereospecific diolefin polymerization by coordination catalysis and ring opening polymerization of oxiranes and lactones by homogeneous catalysis in the presence of mixed oxide catalysts;

— the second group is devoted to the application of *coordination* catalysis to some specific area of organic chemistry: 1) The selectivity and efficiency of carbenes (generated from diazocompounds) have been considerably improved by application of *rhodium* and *palladium* catalysts to typical carbene reactions such as cycloadditions, insertion reactions and *ring enlargement of aromatics*.

Some exploratory work on isocyanates and azides activation will also be reported together with mechanistic informations resulting from kinetics measurements. 2) The specific functionalization of petroleum hydrocarbons is another field of interest: copper catalyzed hydrocyanation of diolefins and specific oxidation of alkanes and olefins in the presence of soluble transition metal complexes have been investigated in this respect together with the preparation of novel cobalt and molybdenum complexes.

The research fields of our group are centered on the application of homogeneous catalysis in two main areas. I. Homogeneous catalysis applied to the control of typical organic reactions such as carbene reactions, novel reaction of heterocumulenes (isocyanate, sulfinylaniline), synthesis of heterocycles, hydrocyanation of olefins and oxidations.

A. Carbene chemistry

Carbenes are important intermediates in organic synthesis and one of the most elegant ways to generate them is to decompose a diazo compound. In fact, we used diazo esters as carbene precursors:

$$N_2$$
CHCOOR $\xrightarrow{d, h\nu}$: CHCOR + N_2

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Copper catalysts are used since a very long time to promote carbene reactions: it is generally accepted that carbene-metal complexes (carbenoids) are the active species.

In fact, our approach was to improve or modify carbene reactions by investigating the catalytic properties of Group VIII metal complexes. A screening led to the discovery of interesting catalytic properties of Pd (II) and Rh (II) carboxylates. Therefore, the most typical reactions of carbenes have been reinvestigated with these catalysts:

- 1 Cycloaddition to olefins to give cyclopropanes;
- 2 Cycloaddition to acetylenes to give cyclopropenes;
- 3 Ring enlargements of aromatics;
- 4 Insertion reactions into O—H, (NH), S—H and aliphatic C—H bonds;
- 5 1,3-dipolar addition to $-C \equiv N$ and =C = N-bonds.

1. Cyclopropanation of olefins

Rhodium led to efficient catalysis of cyclopropane formation from olefins. Even a relatively inactive olefin such as trans 4-octene can be efficiently cyclopropanated with Rh (II) carboxylates [1]. However, the efficiency is the result of a subtle adjustment of the conditions:

- slow addition of the diazo ester to a *dilute* solution of the catalyst in the neat substrate;

— proper groups must be present both on the catalyst and the diazo ester: for example, in the specific case of trans 4-octene, efficient cyclopropanation is only realized when large lipophilic groups are present both on the catalyst $(t-Bu-COO)_4 Rh_2$ and the diazo ester (n-Bu diazoacetate). The yield decreases by a factor of ten when *methyl* groups are present.

In fact, Rh (II) carboxylates are generally not selective in cyclopropanation of differently substituted olefins (as opposed to Pd carboxylates; see later) except in particular cases, e. g. the cyclopropanation of A can be performed with high regioselectivity and the cyclopropane carboxylate B, a precursor of a pyrethroid type pesticide has been obtained in good yield with Rh catalysts:



Palladium catalysis [2]: Pd (II) acetate is less efficient than Rh (II) carboxylates except in the case of activated olefins (such as styrenes) or strained olefins (such as norbornene or norbornadiene).

Moreover, this catalyst is more sensitive to *steric* effects than Rh: increased substitution leads to a sharp drop of the yield.

Both catalysts are obviously acting by two completely different mechanisms (see later).

2. Cyclopropanation of acetylenes

The cycloaddition of carbenes to acetylenes gives cyclopropenes. Copper and palladium catalysts have been reported as being efficient with *disubstituted* acetylenes but "true" acetylenes give rearrangement or polymerization products with these catalysts. In opposition, cyclopropenes are formed in good yields even with the "true" acetylenes by using Rh (II) carboxylates as catalysts [3]. NB: A characteristic of the Rh catalysts is their compatibility with sensitive substrates and products.

3. Ring enlargement of aromatics

The classical Buchner synthesis of cycloheptatriene carboxylates from benzene gives a mixture of positional isomers (corresponding to the thermodynamic equilibrium) and moderate yield. However, Rh (II) trifluoroacetate (triflate) catalyzes the formation of a single isomer with high selectivity (>95%) [4] and in practically quantitative yield. We observed also some regioselectivity with substituted benzene substrates.

4. Insertion of carbenes into X—H bonds

(X = 0, (N), S, C) [5] Rh (II) carboxylates and copper triflate are efficient catalysts for the insertion of carbalkoxycarbenes into alcohols and mercaptans. Even the insertion into aliphatic C—H bond can be realized with high efficiency and some selectivity by using Rh (II) salts of strongly electron-attracting carboxylates (trifluoro-acetates, pentafluorobenzoate . . .) as for the ring enlargement reaction of aromatics. For example, yields close to 90% can be obtained with cyclohexane but the efficiency is strongly temperature dependent: the best yields were obtained close to the boiling point of the hydrocarbon. The deactivation of the catalyst, probably by reduction of Rh (II) to Rh (I), seems to be the result of the decomposition of some diazoester Rh (II) complex formed at low temperatures.

5. 1,3-dipolar addition of carbalkoxycarbenes

A carbalkoxycarbene can react as a 1,3-dipole:



a) Cycloaddition to nitriles occurs easily: oxazoles are formed in good yield particularly with copper triflate and Pd (II) acetate as catalysts.

Moreover, the regioselectivity [6] of attack of acrylonitriles can be thus controlled: the thermal reaction leads to the exclusive attack of the C=C double bond (cyclopropane is formed at 100 °C whereas Δ^2 pyrazoline is formed at 25 °C by cycloaddition of the diazo-group and formation of a Δ^1 , pyrazoline as a transient intermediate which rearranges to the Δ^2 isomer or decomposes to give the cyclopropane, depending on the temperature).



b) 1,3-dipolar addition to a carbodiimide [7] proceeds smoothly in the presence of Rh carboxylate of copper triflate with the formation of imino-oxazoline.

Mechanism of the catalyzed carbene reactions

SALOMON and KOCHI [8] has discussed the occurrence of two mechanistic pathways during the copper catalyzed cyclopropanation of olefins.

1. A classical *carbenoid mechanism* when copper acetyl-acetonate is used as a catalyst: the strong acetylacetonate ligand prevents the coordination of the olefin to the catalytic center:

> (I) $M + N_2 CHCOOR \xrightarrow{-N_2} M = CHCOOR$ $M = CHCOOR + C = C \xrightarrow{-N_2} P$

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2. a coordinative mechanism which can be detected during the early stages of the copper triflate catalyzed cyclopropanation (the CF_3SO_3 group is a very weak ligand and allows the coordination of the olefin to copper),

$$M + \geq c = c \leq + N_2 CHCOOR \longrightarrow M = c \leq H \longrightarrow M = c = H \longrightarrow P$$

Our results can be explained by assuming the *exclusive* participation of the *carbenoid process with Rh (II)* carboxylates and of the coordination pathway with Pd (II). The duality of mechanism appears upon plotting the relative reactivities of olefins against their complexing abilities towards silver. The Pd catalyzed reactions correspond to a widely scattered distribution of the plots: the best coordinating olefin displays, however, the highest reactivity. In contrast, Rh catalysis leads to a narrow range of reactivity and coordination is no more a determining factor in this case.

The structure of the Rh (II) carboxylates explains the results: they are stable dimers containing a single coordination site per Rh.



On the contrary, Pd acetate is a trimer, easily cleaved in solutions, which presents therefore several available coordination sites.

B. Metal carbonyl catalyzed reactions of cumulenes

1. Reaction of isocyanates with aldehydes

 $(Fe(CO)_5, Co_2(CO)_8 [9])$. Imines are formed in good yields from aromatic aldehydes (aliphatic ones give aldol condensation products of the imine).

$$Ph - N = C = O + RCHO \rightarrow Ph - N = CHR + CO_2$$

The kinetics of the reaction is easily followed by volumetry [10]. Kinetic measurements show the slow formation of the true catalytic species. The partial orders are different: zero in isocyanate, one in aldehyde. The catalytic cycle is explained by the following scheme:



2. Reaction of sulfinylaniline with isocyanates [11]



The reaction proceeds through the formal cyclocondensation of two isocyanate and one nitrene moiety (formed from Ph=N=S=0 and the catalyst).

3. Reaction of azides with aldehydes

Amidoderivatives are formed from aldehydes and benzyl azide in the presence of a metal carbonyl



C. Hydrocyanation of conjugated olefins

Hydrocyanation of butadiene is a very important industrial process. DU PONT has devised an efficient synthesis of adiponitrile (a nylon-6,6 precursor) from the nickel(O) catalyzed hydrocyanation of butadiene:



Copper catalysis is also claimed as an efficient process in the patent literature.

Our study [12] in that field shows that the copper catalyzed hydrocyanation is strictly limited to the monoaddition step (a). Moreover copper halides are the only active species. Activation of the inactive CuCN catalyst can however be promoted by addition of crotyl bromide: the catalytic system thus obtained is even more active than cuprous bromide. In fact, halide containing promoters can accelerate the reaction (e.g. BrCN, and mainly an allylic bromide such as crotyl bromide, a potential intermediate in the reaction). We have proposed the following scheme:



D. Oxidation of olefins and hydrocarbons

Oxidation of cycloalkanes and cycloolefins by Co (III) acetate (a stoichiometric reaction) has also been investigated in our laboratory [13].

It is reported that this oxidation selectively occurs at the 2nd position of linear alkanes [14] and that even a tertiary CH bond is less reactive than a secondary one. Steric effects are obviously acting as we observed that with adamantane the (less hindered) tertiary C—H bond is more reactive than the CH_2 groups.

The mechanism involves oxidation of a Co (II)-radical complex by a second Co (III) acetate molecule [14]. *Catalytic oxidation* of cycloolefins by mixed catalysts (Rh carboxylates associated with a V or Mo epoxidation catalyst) led to the formation of epoxides with the Mo catalyst and epoxyalcohols with VO(acac)₂ [15].

The mechanism involves the Rh catalyzed radical formation of cycloalkenyl hydroperoxide, which acts as an epoxidation agent towards the double bonds.

II. Coordination catalysis applied to polymer chemistry

The stereoselectivity of butadiene polymerization has been controlled by using soluble π -allyl nickel catalysts. Another aspect studied in the group is the ring-opening polymerization of epoxides and lactones in the presence of soluble bimetallic oxide catalysts.

A. Polymerization of butadiene

The polimerization of butadiene can classically follow three different routes:

(1) 1,4-cis-polymerization,

(2) 1,4-trans-polymerization,

(3) 1,2-polymerization,

 π -allyl metal catalysts can catalyze very selectively these different polymerization modes of butadiene: Cr and Mo catalysts lead to 1,2-polybutadiene (>95%), whereas Ni and Co complexes give 1,4-cis- or trans-polybutadiene (selectivity >98%).

If the nature of the metal is an important factor, it is noteworthy that the selectivity of a metal can be very deeply modified by the use of different *ligands*. For example, in the particular case of π -allyl nickel, the stereoselectivity can be changed from 98% 1,4-*cis* to 99% 1,4-*trans* by using different counterions on the nickel complex:



X, % cis to trans: CX₃COO (98:1), Cl (85:14), Br (65:33), I (--:99). It is, however, possible to achieve an even higher degree of control of

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the stereoselectivity by acting on the environment of the catalytic center: the *ligands* and the *solvent* can determine the selectivity.

The originality of the contribution of Liège in this field has been to find the factors allowing the control of the distribution of *stereoblocks within the polymer chains* [16].

 π -allyl Ni trifluoracetate gives cis-1,4-polybutadiene (99%) in paraffins as solvent.

Addition of an equimolar amount (relative to the metal) of phosphite $P(OR)_3$ or alcohol reverses completely the selectivity (99% trans).

In aromatic solvents or in dichloromethane, an equibinary polymer is obtained: the chains contain a 1:1 ratio of cis and trans double bonds.

Addition of trifluoroacetic group to the catalyst in paraffinic solvent modifies the *cis*-selectivity towards the equibinary distribution.

Moreover, π -allyl nickel complexes can be used as *coding catalysts* for equibinary 1,4-butadiene polymerization: different mean block lengths can be adjusted by changing the solvent.

(4)

N. B: polymerization in benzene leads to a statistical distribution of *cis* and *trans* double bonds, the distribution is close to a regular alternating sequence in chlorinated solvents (as shown by 300 MHz H-NMR spectroscopy).

The mechanism

The *cis*-polymerization is the result of a bidentate coordination of butadiene in the *cisoid* conformation to *two* coordination sites of nickel, whereas the *trans* control of the microstructure is achieved through the *monodentate* coordination of butadiene on *a single* coordination site. The equibinary polymer results from the kinetic control of both site activity by a delicate balance of solvation: the dormant species is in fact a dibridged dimer: opening of one bridge gives the active species which presents the two sites controlling the microstructure of the polymer:



Application

Preparation of block copolymers. The π -allyl nickel catalyst is a living catalyst, the growing chain remains linked to the metal center. Therefore, it is

possible to start a novel polymerization by adding butadiene after consumption of the first amount. If a ligand (phosphite) is added prior to this novel butadiene addition, then the stereocontrol of the polymer (purely *cis* in a paraffin) will be reversed during the second stage: block *trans* can thus be linked to block *cis*.



Diblock copolymers can be elaborated from: 1,3-diene — 1,3-diene stereoblocks 1,3-diene — styrene ethylene — styrene Multistereoblock: poly(cis-trans)_n 1,4-butadiene.

B. Ring opening polymerization of epoxides and lactones

Epoxides and lactones are readily polymerized on mixed oxide catalysts to give polyethers and polyesters [17]. The product of propylene oxide polymerization contains a soluble fraction of atactic oligomers (\sim 12-mer statistical opening) and less soluble isotactic high polymer (97%, MW 10⁶) corresponding to a stereospecific ring opening. The standard catalyst used for these studies is easily prepared by heating aluminium alkoxide and zinc acetate (2 : 1) in decaline at 190% C for the time necessary to recover the alkylacetate (several hours):



Carefully controlled hydrolysis of the mixed 2Al-Zn alkoxides is a method for catalyst preparation at room temperature. Catalysts can be prepared from various metals: Zn, Co, Cr, Fe, Mo, Al, Ti.

These complexes exist as aggregates (n = 1 - to 10) depending on the solvent, the nature of the metals and of the alkoxy groups.

The Al-Fe, Al-Mo and Al-Cr complexes absorb oxygen readily to form metal-oxygen complexes with different stoichiometries $(M: O_2) = 1:1$ (Mo), 2:1 (Fe, Cr).

III. Complex chemistry

Some unusual complexes have been obtained during these studies (see structures C and D) [18, 19].



 $\mathbf{R} = i \cdot \mathbf{Pr}$

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PREPARATION OF HIGH SURFACE AREA TUNGSTEN CARBIDE*

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The aim of the series of investigations we have undertaken is to gain a better understanding of how various parameters of tungsten carbide preparation may influence its activity as a catalyst. The variables investigated were the nature of the porous hydrous oxide, presence of additives, and stoichiometry of the compound.

Several methods of preparation of tungsten oxides were investigated. The reactivity of these oxides towards hydrogen and CO or CO/CO_2 was also studied. The nature of the precursor and its Na content were studied as parameters which influence the reactivity of the solid. For a complete understanding of the reactivity, thermodynamic factors were considered.

Introduction

In 1973, BOUDART [1] forecasted that tungsten carbide might possess some interesting properties relevant to heterogeneous catalysis. His reasoning was based on the fact that the electronic structure of tungsten carbide (WC) resembles those of platinum.

Additionally, the work of BÖHM et al. [2, 3, 4] showed the efficiency of tungsten carbide as a catalyst for the oxidation of hydrogen. Its lack of sensitivity to poisons, such as CO and H₂S, increased interest in this new solid [5, 6].

Several authors have shown the strong influence [7-15] of the method of preparation of tungsten carbide on its catalytic activity. In particular, the method of preparation of the precursor oxide would appear to be a dominant step in determining the final catalytic activity of tungsten carbide.

The traditional method of preparation of WC comprises essentially three steps: preparation of the precursor oxide, reduction to the metallic state and carburization.

Tungsten oxide exists in two forms: the white and the yellow modifications. The former is prepared [18] from hot solutions of concentrated acids and tungstates, while the latter from cold solutions of dilute acids and tungstates.

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Thus the aim of this work was to explore different methods of preparation of tungsten carbide to be able to control the specific surface area, the texture and the chemical composition of WC.

Experimental

Preparation of $(NH_4)_2WO_4 - (T. A.)$

The stoichiometric quantity of H_2WO_4 was added to an aqueous solution of NH_3 under mixing. The mixture was refluxed for 10 min. After cooling to 25 °C, the solution was freezedried. Ammonium tungstate, very soluble in water, was thus obtained.

Preparation of tungsten hydrous oxides

Preparation from $Na_2WO_4 \cdot 2H_2O$

a) Yellow modification

A 0.267 M solution of $Na_2WO_4 \cdot 2H_2O$ was acidified with 1N nitric acid to pH 5.5. 1N nitric acid was then added to that stock solution to pH 0.4. After 30 min of reaction at 25 °C, the solution was deposited in a furnace at 60 °C for 4 hrs.

b) White modification

The stock solution was acidified to pH 1.4. This solution was then directly deposited in a furnace held at 90 $^\circ$ C for 4 hrs.

Preparation from (NH₄)₂WO₄

a) Yellow modification

A 0.01 M solution of T. A. was acidified with 1N nitric acid to pH 0.35. Thereafter, the procedure was as described above (preparation from $Na_2WO_4 \cdot 2H_2O$).

b) White modification

A 0.05 M solution of T. A. was acidified with 0.1N nitric acid to pH 0.6. The procedure then was as described above (preparation from Na₂WO₄ · 2H₂O).

Drying of hydrated oxides

After cooling to ambient temperature, the samples were rinsed with distilled water, separated by centrifuging at 5000 r.p.m. for 10 min. The supernatant was eliminated and the solid was again suspended in distilled water. Each precipitate was washed 3 times in this manner. Finally the solid was redispersed in distilled water and the suspension was freezedried in a VIRTIS freeze mobile 12 apparatus.

Preparation of ammonium tungstate (T. A.) by lyophilization

A 0.1 M solution of T. A. was injected through a capillary tube into liquid hexane which was cooled to -30 °C. After filtration, the solid, which was in the form of microdrops, was freeze-dried.

Preparation of sodium containing samples

The desired amount of $NaNO_3$ was added to a solution of T. A., prepared as described above. After freeze drying, this procedure yields solid T. A. doped with Na. It is noteworthy that the Na thus introduced was incorporated quantitatively into the hydrated oxides obtained by precipitation even after these materials had been washed several times.

Materials

High purity H₂WO₄(WCB) and Na₂WO₄ · 2H₂O (MERCK) were used as received.

Thermal treatment

The oxidic precursor of tungsten carbide prepared by the methods outlined above was first reduced under hydrogen and then carburized under CO or CO/CO_2 .

Generally, 0.5 to 1 g of oxidic precursor was supported on glass wool and held in a fixedbed reactor. Flows of H_2 or CO gas, after purification by passage through a bed of molecular sieve (5 Å), could then be directed at the desired temperatures over the solid. This arrangement ensured good contact between the solid and the gas phase.

The reduction of oxidic precursor was carried out under a flow of H_2 (15 L/h) and the temperature of the solid was raised from ambient to 500 °C at a rate of 1 °C/min. After the oxide has been reduced for the desired length of time, the H_2 flow was replaced with an argon flow and the solid held at 500 °C under Ar for one hour. To examine the intermediate metallic tungsten, the oven was cooled to room temperature and the solid passivated under a flow of 5% O₂/He at 25 °C for 2 h. Without this passivation treatment, the tungsten intermediate combusted spontaneously in air. It was verified that this passivation treatment modified neither the structure nor the specific surface area of the product.

After reduction and storing under Ar, CO at a flow rate of 20 L/h was passed over the solid and the temperature was raised at the desired rate to the carburization temperature. After carburization for the desired length of time, the CO was replaced with an Ar flow cooled to ambient temperature and passivated under 5% O₂/He at 25 °C for 2 h.

Gas

 $H_2(N30)$, CO(N37), CO₂(N45), Ar(N46) were used as supplied by AIR LIQUIDE without any further purification.

Analytical methods

a) X-ray diffractometry

X-ray diffractograms of solids were recorded on a Philips PW 1051 apparatus using K_{α} Cu radiation (= 1.5418 Å) filtered through Ni.

b) Specific surface areas were measured on a vacuum microbalance by the B. E. T. method using N_2 as adsorbate at 77 K.

c) Electron microscopy

Samples were suspended in high purity methanol and dispersed by ultrasound. A drop was deposited on an AEI grid with carbon support.

Transmission electron micrographs were obtained on an AEI EM6 G microscope using an acceleration voltage of 100 kV.

Scanning electron micrographs were recorded on a JEOL TEMSCAN 100 CX (acceleration voltage 60 kV).

d) Temperature Programmed Reduction (TPR)

TPR of oxides was carried under H2 in an apparatus already described in full details [22].

Results

Oxides prepared from Na₂WO₄

X-ray diffractograms recorded before and after lyophilization indicated that the yellow modification was $WO_3 \cdot H_2O$ (ASTM file 18 · 1418), whereas the white modification was the hexagonal form of tungsten oxide [20]. After calcination at 500 °C in air for 4 h, the transformations of $WO_3 \cdot H_2O$ and hexagonal WO_3 to the orthorhombic form of WO_3 were complete. However, the X-ray diffractogram of WO_3 (orthorhombic form) was modified by the appearance of an additional peak at d = 3.14 Å.

Specific surface areas of the oxide precursors calcinated at different temperatures are presented in Table II.

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100				-
	'n	b	0	
	a		UC.	

Atomic absorption analysis of the Na content of different precursors

Starting salt	Precursor	Na content (wt%)
$Na_2WO_4 \cdot 2H_2O$	WO ₃ hexagonal	1.7
	$WO_3 \cdot H_2O$	1.6
$(\mathrm{NH}_4)_2\mathrm{WO}_4$	$WO_3 \cdot 1/3 H_2O$	0
	$\mathbf{WO}_3\cdot\mathbf{H}_2\mathbf{O}$	0

Analysis by atomic absorption of the Na content of each sample is presented in Table I.

Oxides prepared from $(NH_4)_2WO_4$

X-ray diffractograms run before and after freeze-drying showed characteristics of both $WO_3 \cdot 1/3 H_2O$ and $WO_3 \cdot H_2O$. The peaks at d = 3.671 Å and 3.31 Å are characteristic of the former, whereas the remaining peaks of the latter compound.

After 5 h of calcination at 500 °C, X-ray diffractograms intermediate between that of (hexagonal) WO₃ and (orthorhombic) WO₃ were observed.

Before and after freeze-drying, the yellow modification was identified as $WO_3 \cdot H_2O$. After calcination at 500 °C, the transformation into WO_3 (orthorhombic) was complete.

The specific surface areas of the two oxides calcinated at different temperatures are presented in Table II.

The morphology of these oxides is shown in Fig. 1. The particles are in the form of fine needles for $WO_3 \cdot 1/3 H_2O$ and in the form of platelets for $WO_3 \cdot H_2O$.

Table II

Specific surface areas $(m^2 g^{-1})$ of the different precursors for the calcination temperature indicated

Starting salt	n	Temperature (°C)			
	Precursor	25	300	500	
$Na_2WO_4 \cdot 2H_2O$	WO ₃ hexagonal	$70\!\pm\!2$	_	21	
	$WO_3 \cdot H_2O$	$26\!\pm\!0.2$	-	10.5	
$(\mathrm{NH}_4)_2\mathrm{WO}_4$	$WO_3 \cdot 1/3 H_2O$	82 ± 2	85.7	36	
	$WO_3 \cdot H_2O$	$16{\pm}0.1$	26.3	13.3	
	T.A. (lyop)	5	-	5.2	

N. B.: The errors indicate variations observed in specific surface area between different preparations



Fig. 1. Morphology of WO₃ \cdot 1/3 H₂O(A), WO₃ \cdot H₂O(B) and (NH₄)₂WO₄ prepared by freezedrying (C)

Results of atomic absorption analysis for the sodium content of the samples are presented in Table I.

Preparation of T. A. by lyophilization

This solid prepared by lyophilization was amorphous at 25 °C. After calcination at 500 °C (one night), it was transformed to WO_3 (orthorhombic form). The specific surface areas of samples of this solid calcinated at 25 °C and at 500 °C are presented in Table II and their morphology is shown in Fig. 1.

Influence of the nature of the oxidic precursor and of the sodium content on the reactivity, specific surface area and morphology of the product tungsten

The TPR patterns of $WO_3 \cdot 1/3 H_2O(A)$, $WO_3 \cdot H_2O(B)$ and of ammonium tungstate obtained by freeze-drying are presented in Fig. 2. The reduction temperature of $WO_3 \cdot H_2O$ was lower than that of $WO_3 \cdot 1/3 H_2O$.

Table III presents the specific surface areas of the various metallic tungstens obtained by reduction of the three precursor oxides for sodium content of 0 and 1.6 wt%.

Influence of carburation temperature, nature of the precursor oxide and the carburation atmosphere

Table IV presents the experimental conditions used to achieve carburization of various samples. The samples had been previously reduced under



Fig. 2. TPR patterns of samples prepared by homogeneous precipitation from ammonium tungstate; a: $WO_3 \cdot 1/3 H_2O$, b: $WO_3 \cdot H_2O$, c: $(NH_4)_2WO_4$

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Table III

Precursor	Na content (wt%)	Specific surface area (m ¹ g ⁻¹)
$WO_3 \cdot 1/3 H_2O$	0	71
	1.6	4.4
$WO_3 \cdot H_2O$	0	64
	1.6	57
T.A. (lyoph.)	0	5.2
	1.6	32

Specific surface area $(m^2 g^{-1})$ of the metallic tungsten obtained by reduction of the oxidic precursors prepared from ammonium tungstate with and without sodium

Table IV

Attempts at carburization at different temperatures and under different atmospheres of samples of metallic tungsten obtained by reduction of $WO_3 \cdot 1/3 H_2O$ and $WO_3 \cdot H_2O$

Experi- ment number	Precursor oxide	Temperature rate (°C min ⁻¹)	Increase gas	Reac- tion temp. (°C)	Reaction gas	Reac- tion time (hrs)	% W2C	wc	Spec. surface area (m ² g ⁻¹)
1	$WO_3 \cdot 1/3H_2O$	1	со	750	со	6	75	25	54
2	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	1	CO	750	CO	12	53	47	54
3	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	1	CO	750	CO	24	72	28	50
4	$\mathrm{WO}_3 \cdot \mathrm{1/3H_2O}$	1	CO	850	CO	6	47	53	30
5	$WO_3 \cdot 1/3H_2O$	1	CO	850	CO	12	0	100	47
6	$WO_3 \cdot H_2O$	1	CO	750	CO	6	81	19	50
7	$\mathrm{WO}_3 \cdot \mathrm{H_2O}$	1	CO	750	CO	24	0	100	38
8	$WO_3 \cdot H_2O$	1	CO	850	CO	12	4.4	56	1
9	$\mathrm{WO}_3 \cdot \mathrm{1/3H_2O}$	1	CO/CO_2	750	CO/CO_2	24	100	0	38
			1/1		1/1				
10	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	1	CO/CO ₂	850	CO/CO ₂	12	W	O_2	1
			1/1		1/1				
11	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	5	Ar	722	CO/CO ₂	3	100	0	/
					1/1				
12	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	5	Ar	722	CO/CO ₂	24	100	0	1
					1/1				
13	$\mathrm{WO}_3 \cdot 1/3\mathrm{H_2O}$	5	Ar	780	CO/CO_2	6	48	52	1
					10/1				
14	$WO_3 \cdot 1/3H_2O$	5	\mathbf{Ar}	780	CO/CO ₂	12	0	100	1
					10/1				

 $\rm H_2$ at 500 °C for 5 h. The final degrees of transformation calculated on the basis of the most intense X-ray diffractogram peaks for WC and W₂C, are presented in columns 8 and 9 of this Table.



250 nm





Fig. 3. Morphology of tungsten carbide prepared by reduction and carburization of $WO_3 \cdot 1/3 H_2O(A)$ and of $WO_3 \cdot H_2O(B)$

In the case where the precursor oxide was $WO_3 \cdot 1/3 H_2O$, carburized at 750 °C under pure CO, a diminution in the % yield of WC was observed for carburization times in excess of 12 h, as compared to the yield obtained for times less than 12 h (experiences 2 and 3). No such drop of WC formation was observed with $WO_3 \cdot H_2O$ as the precursor oxide. At 850 °C, transformation of W_2C and $WO_3 \cdot 1/3 H_2O$ into WC was complete. In the case of $WO_3 \cdot H_2O$, carburized at 850 °C for 12 h, only a partial transformation was achieved (expts. 5 and 8).

Figure 3 shows two samples of WC obtained by reduction of $WO_3 \cdot 1/3 H_2O(A)$ and $WO_3 \cdot H_2O(B)$ followed by carburization under CO. The former was composed of well-separated fine grains, whereas the latter was composed of square platelets showing pronounced surface roughness.

Discussion

The method of homogeneous precipitation allowed us to prepare 2 oxide precursors both crystalline in nature but possessing different textural properties, both oxide precursors were in the form of extremely fine powders.

The white modification possesses a morphology similar to $WO_3 \cdot 1/3 H_2O$ described recently by GÉRAND *et al.* [21]. The higher state of dispersity formed in this work, 80 m² g⁻¹ as compared to 23 m² g⁻¹ for the GÉRAND preparation, can be explained by the different methods of preparation used. GÉRAND *et al.* prepared their oxide by hydrothermal treatment of a gel at 120 °C for 20 hrs in an autoclave.

The classic method of oxide precursor preparation outlined by KULCIS- KY [18] results in oxides of specific surface areas varying between 5 and 80 m² g^{-1} , depending upon the experimental conditions. The method of preparation of colloidal tungsten oxide by homogeneous precipitation permits the preparation of two precursors in a very dispersed state, in a very reproducible manner, in particular with regard to their specific surface areas. The use of 2 ageing temperatures depending on which type of precursor was desired, 60 or 90 °C, allowed on increase of the specific surface area of $WO_3 \cdot 1/3 H_2O$ by a factor of 2 and ensured that $WO_3 \cdot H_2O$ had a more homogeneous morphology [13].

T	a	b	1	e	V
-			-	~	

Specific surface areas $(m^2 g^{-1})$ of the two modifications of the precursor oxides prepared from Na_2WO_4 at the ageing temperature indicated

Ageing temperature (°C)			
60	90	110	
_	80	38	
16		38	
	Agein 60 16	Ageing temperature 60 90 — 80 16 —	



Fig. 4. Relation between the wt% content of Na in oxide precursors prepared by hot petroleum and the intensity of X-ray diffraction peaks as the ratio of $I_{28,4^\circ}$ and $I_{28,4^\circ}$ (2 Θ)

When using ammonium tungstate in place of sodium tungstate, the loss of specific surface area observed during calcination of the latter was largely inhibited (Tables II and III).

A second advantage of the former precursor salt was to allow introduction of promoters into the solid. It should be recalled that upon addition of Na to a solution of T. A. before freeze-drying, the promoter was found to have been incorporated quantitatively into the precipitated oxide.

Influence of sodium

One of the first effects brought about by additon of Na was the modification of X-ray diffractograms of the samples after calcination at 500 °C. The reduction in intensity of the peak at $2\Theta = 28.8^{\circ}$ in the diffractogram of orthorhombic WO₃ and the appearance of a new peak at 28.4° whose intensity increased with the sodium content can be explained by the progressive formation of a sodium tungstate bronze (Na_{0.1}W_{0.9}O₃). We have presented in Fig. 4 the relation between the intensity of peaks at d = 3.14 Å and d == 3.09 Å and the wt% content of Na in the sample. Since a linear relationship was observed for samples of WO₃ calcinated at 500 °C, an estimation of the Na content can be obtained from their X-ray diffractograms.

The influence of the addition of Na to an extent less than 0.5% has yet to be studied.

Gas-solid reactions

The high state of dispersity of $WO_3 \cdot 1/3 H_2O$ gave rise to hopes that its reactivity with respect to H_2 would be greater than the reactivity of the less dispersed $WO_3 \cdot H_2O$.

TPR analyses showed that the latter could be reduced at a lower temperature than $WO_3 \cdot 1/3 H_2O$. Upon examination of Table II, it can be clearly seen that at 300 °C (temperature of dehydratation of $WO_3 \cdot H_2O$) the specific surface area of this material increases. Pore formation during the departure of water from this material can then partially explain the higher reactivity of $WO_3 \cdot H_2O$. The second part of the explanation arises from the transformation of the two oxides during the temperature increase. In the process of loosing the water of hydratation, $WO_3 \cdot H_2O$ transforms at 300 °C into (orthorhombic) WO_3 , whereas $WO_3 \cdot 1/3 H_2O$ transforms at 400 °C into the hexagonal phase of WO_3 . The different structures between the phases which react with H_2 thus also contributed to the differences in reactivity observed.

Carburization of metallic tungsten

In the absence of free carbon, *i.e.* where there is good contact between the solid and gas phases, the thermodynamic phase diagrams indicate that in the temperature range of 750 to 850° C, WC is stable (Fig. 5).



Fig. 5. Phase diagram for the system $WC/W_2C/WO_2/WO_3$ featuring the ratio pCO_2/pCO and the reciprocal absolute temperature. The numerical values used are those given by BARIN and KNACKE assuming that the total pressure of CO = 1 atm



Fig. 6. Phase diagram for the system $WC/W_2C/WO_2/WO_3/C$ featuring the ratio pCO/pCO_2 and the reciprocal absolute temperature assuming that the partial pressure of CO is equal to (1): 1 atm, (2): 2/3 atm, (3): 0.5 atm

However, deposition of carbon formed by dismutation of CO, according to the BOUDOUARD reaction, can cover and isolate the tungsten particles from the reaction atmosphere.

We must therefore envisage reactions in the solid phase and in such a case new domains of stability appear (Fig. 6).

In this case W_2C is the only tungsten carbide stable at 850 °C. However, at 750 °C WC is the only stable phase.

Examination of Table IV reveals that the transformation of W into W_2C is fast and occurs under any reaction conditions. We can therefore propose the following reaction scheme:

Taking into account these data, we can attempt to explain the blocking and regression observed in experiments 2 and 3 of Table IV. As indicated in Fig. 3 tungsten derived from $WO_3 \cdot 1/3 H_2O$ consists of small, well-separated grains; this morphology does not change during carburization. Thus at 750 °C, carbon deposits into the grains, isolating the grain from the gas phase and interfering with the transformation of W_2C to WC. One possible explanation of the retardation of this reaction can be found in the fact that the interfacial

energy for the system WC/W_2C makes the WC phase unstable thus provoking the transformation: $2WC \rightarrow W_2C + C$.

The texture of WC originating from $WO_3 \cdot H_2O$ was totally different (see photo B in Fig. 3). The porosity of these particles would allow the penetration of CO_2 into the interior of sufficiently large pores thus inhibiting the dismutation reaction of CO and allowing the transformation of W_2C to WC to be completed.

Increasing the carburization temperature from 750 to 850 °C increased the rate of diffusion of carbon in the tungsten crystallites (activation energy 40.4 kcal mol⁻¹) twice as much as the rate of carbon formation on the surface of the solid (activation energy: 20.2 kcal mol⁻¹). Thus at 850 °C, W derived from WO₃ \cdot 1/3 H₂O was completely transformed to WC (exp. 5). In the same conditions, carburization of W from WO₃ \cdot H₂O was incomplete (exp. 8). Several reasons may be proposed to explain this latter finding.

1. The increase of the temperature would not markedly affect diffusion processes in the gas phase. Thus the reaction rate may become limited by mass transfer effects.

2. As explained above, the presence of CO_2 could inhibit the carburization reaction.

3. The larger particle size associated with W from $WO_3 \cdot H_2O$ could render it less active.

The results of carburization experiments carried out in a mixture of CO and CO_2 can be readily explained on the basis of the thermodynamic equilibrium phase diagram presented in Fig. 6.

The stability domains which were determined by the experimental conditions used for experiments 9 and 10 (Table IV) explain these results. The inhibition of the reaction at the intermediate W_2C stage observed in experiments 11 and 12 (Table IV) can be readily explained on the basis that the solid

Precursor	Specific surface area	Ref.	
W metal.	2 to 4		
WCl ₆	3 to 5	[22]	
White modif.	5.5 to 15.7	[15]	
Yellow modif.	3.7 to 11.8		
W metal.	30	[16]	
Tungstic acid	32	[17]	
White modif.	5 to 15		
Yellow modif.	15	[6]	

Table VI

Specific surface areas of WC reported in the literature

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Sample	Specific surface area (m ² g ⁻¹)	Density (g cm ⁻³)	D (Å)	Spec. surface area SiO ₂ (m ² g ⁻¹) ^(a)
$WO_3 \cdot H_2O$	16	7.16	524	52
$\mathrm{WO}_3 \cdot 1/3 \ \mathrm{H_2O}$	80	7.16	105	260
W ex yellow mod.	64	19.3	49	1235
W ex white mod.	71	19.3	44	1370
WC	50	15.6	77	355

Comparison of the degree of dispersity of WC and intermediate compounds with silicas of equivalent particle shape and size

Table VII

^a Specific surface area calculated from $S = \frac{6}{\overline{D} \mathbf{x} \varrho}$ where ϱ is the density of silica

was exposed to an excess of CO_2 . In fact, the correct choice of the CO/CO_2 ratio allowed not only that the reaction could proceed to completion (see expts. 13 and 14) but to proceed at a higher rate than in pure CO.

Dispersion of carbides and intermediates

Tables VI and VII compare data for specific surface area for W compounds taken from the literature with the values measured in this work. To obtain a deeper understanding of the state of dispersion obtained with our samples, it is necessary to recall that both W and WC have very high density. Table VII presents measured values of specific surface area for different tungsten compounds prepared in this study. This Table also presents the grain size calculated on the basis that all solid particles are spherical. This Table also presents the specific surface areas which would be associated with silica in the form of identically sized spherical particles. Thus the states of dispersion attained for W and its carbide are comparable with those obtained for the most highly dispersed silicas.

Conclusions

The method of preparation of hydrated oxides of tungsten from $(NH_3)WO_4$ has enabled us to prepare two precursors of WC. These precursors are different in their crystalline and textural properties, are free of impurities and in an highly powdered state.

Addition of more than 0.5 wt% in Na caused the recrystallization of the oxide and large modifications in textural properties.

Examination of thermodynamic data allowed explanation of the carburization treatment data and showed the advantages of using a CO/CO₂ mixture to effect this treatment. In particular, the formation of a layer of free carbon (by the BOUDOUARD reaction) blocked and retarded the carburization process. This effect appeared at different instances depending upon the temperature and the texture of the solid. The use of a properly chosen mixture of CO and CO₂ caused acceleration of the carburization reaction at the expense of the rate of formation of free carbon.

The degree of dispersity obtained for W and WC was close to those normally reported for the most highly dispersed silicas.

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TRANSFORMATION OF 1-BUTENE OVER MOLYBDENA-, TUNGSTA-, AND RHENIA-ALUMINA CATALYSTS*

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The transformation of 1-butene was studied in a flow system over $\text{Re}_2O_7/\text{Al}_2O_3$, $\text{MoO}_3/\text{Al}_2O_3$, $\text{WO}_3/\text{Al}_2O_3$, $\text{WO}_3/\text{Al}_2O_$

Introduction

The recognition of the correlation between the isomerization and metathesis of olefins over supported transition metal oxide catalysts is of great importance. Already as early as in 1967 BRADSHAW et. al. [1] reported the increase of the selectivity for $C_2 + C_6$ olefin formation in 1-butene metathesis over a $CoO \cdot MoO_3/Al_2O_3$ catalyst upon poisoning the isomerization activity of the catalyst with incorporation of Na ions. Similar increase of selectivity in metathesis of 1-octene, 2-octene and 3-heptene on molybdena-alumina catalyst upon poisoning it with potassium hydroxide was obtained by CRAIN [2]. KOBYLINSKI and SWIFT [3] found that the double bond isomerization, leading to low selectivity of metathesis on molybdena-alumina, can be best suppressed by thallium ions. A good correlation was observed by them between the concentration of thallium ions in the solution used for the poisoning of the catalyst and both the acidity of the catalyst determined by adsorption of ammonia and the selectivity in metathesis of 1-butene and 1-octene.

Decreasing acidity of the molybdena-alumina catalyst and its increasing selectivity in olefin metathesis can be attained by poisoning it with alkali or alkaline earth metal ions, but this treatment decreases the activity of the cat-

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alyst in the metathesis as well. An improvement of selectivity in 1-octene metathesis by residue formed during the pretreatment of the molybdena-alumina with 1-butene was described by KOBYLINSKI and SWIFT [4]. No metathesis activity was observed initially with molybdena-alumina and rhenia-alumina catalysts by OLSTHOORN et al. [5, 6]. Metathesis activity of the catalysts was induced gradually by contacting them with reactants. Similar induction was described by HALL et al. [7, 8]. Over freshly oxidized molybdena-alumina, isomerization of cis-2-butene proceeded via carbenium ion intermediates [9], metathesis was not observed at all. In the induction period the acidic isomerization decreased concomitant with the increase of the cis-trans transformation via metathesis. Both OLSTHOORN et al. [5, 6] and HALL et al. [7, 8] correlated the induction of metathesis activity with the reduction of the transition metal oxide by the reactant olefin.

According to LAVERTY *et al.* [10], interaction between coordinatively unsaturated transition metal ions and hydroxy groups of the carrier may result not only in Brönsted acid sites, but alternatively in surface metal hydrides:



These surface metal hydrides were proposed to be the initiators for carbenes which are hypothetical intermediates in olefin metathesis. The oxidative addition requires ions in low oxidation state and the presence of a donor ligand such as an alkene already on the metal.

The formation of metal hydrides and carbenes may be preferred if the Brönsted acid sites of the catalysts are poisoned. Such results were reported by VAN ROOSMALEN and MOL [11]; an extensive increase of the metathesis rate of propene over WO_3/SiO_2 was observed by them after the Brönsted acidity of the catalyst was poisoned specifically with hexamethyldisilazane.

Over molybdena-alumina catalysts reduced with hydrogen this reverse correlation between isomerization and metathesis was described in the opposite direction by ENGELHARDT [12]. Metathesis was suppressed but isomerization of butenes enhanced by hydrogen adsorbed at high temperature.

The inverse correlation between isomerization and metathesis reported by VAN ROOSMALEN and MOL [11] and ENGELHARDT [12] can be experienced in the case of different transition metal oxides on the same carrier under similar reaction conditions [13]. Over unreduced $\text{Re}_2O_7/\text{Al}_2O_3$, $\text{MoO}_3/\text{Al}_2O_3$ and

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 WO_3/Al_2O_3 catalysts the metathesis of 1-butene decreases, but its isomerization increases in the sequence given.

The aim of the present work is to shed some light on the correlation between isomerization and metathesis of olefins over different alumina supported transition metal oxides.

Experimental

Catalysts consisting of 4×10^{20} metal atom/g Al_2O_3 (approximately 7% metal/ Al_2O_3) (Ketjen CK 300 γ - Al_2O_3 ; particle size 0.2-0.4 mm) were prepared by impregnation. The adequate quantity of molybdic acid and rhenium heptoxide were dissolved in a volume of dilute ammonium hydroxide equal to the pore volume of the alumina, then the impregnation was carried out in a single step. Multiple step impregnation was applied in preparation of the tungsta-alumina catalyst. In a single step the alumina was impregnated with a fraction of the saturated solution of ammonium (para) tungstate in distilled water. The impregnation was repeated until the catalyst contained the adequate amount of tungsten; between the individual steps it was dried at 393 K and calcined at 773 K. After impregnation each catalyst was dried and calcined for 24 h at the same temperature.

Experiments were carried out in a flow system by using the same charge of catalysts containing 1 g of alumina. Between the experiments the catalysts were regenerated in a stream of purified oxygen at 823 K for 1 h followed by evacuation at room temperature for 1 h. According to our experimental results, the rates of reaction after regeneration were reproducible to within $\pm 5\%$.

1-Butene (Fluka, purum), was purified by freezing, evacuation and distillation, it contained less than 1% impurity (isobutane, *n*-butane, 2-butene).

The reactions were carried out in a quartz reactor at atmospheric pressure between 323 and 523 K at a constant space velocity of 6.9×10^{-6} mol 1-butene s⁻¹ gÅl_{zOa}. Product composition was determined by gas chromatography using a 4 m long column with 20% dibenzylamine / Chromosorb P packing; a flame ionization detector was applied. After the emergence of the butene peaks, pentene and hexene were eluted by increasing the carrier gas flow rate.

Infrared spectroscopic study of the alumina carrier and the catalysts was carried out using a Perkin Elmer 577 double-beam grating spectrometer. Films of $8-18 \text{ mg cm}^{-2}$ "thickness" were pressed and placed into the cell having a calcium fluoride window. The films in the cell were treated with purified oxygen at 266 kPa, at 773 K for 1 h, followed by evacuation at room temperature for 1 h. Then the films were exposed to 1.3 kPa pyridine at 473 K for 0.5 h, and were pumped at the same temperature for 1.5 h. The infrared spectra were determined at room temperature in the frequency ranges of 1400-1700 and 2600-3800 cm⁻¹, respectively.

Similar experiments were carried out on separate films when prior to the adsorption of pyridine the catalysts were treated with 26.6 kPa of 1-butene at room temperature for 20 min and evacuated at the same temperature for 0.5 h.

Results and Discussion

Over freshly oxidized molybdena-alumina catalysts, isomerization of *n*-butenes was found to be proton catalyzed *via* a 2-butylcarbenium ion intermediate [9]. Using *cis*-2-butene as reactant, the acidic isomerization decreased significantly upon contacting the catalyst with butene and transformation *via* metathesis became the prevailing process [7]. The change in the character of the catalyst could be recorded only by using a mixture of *cis*-2-butene labelled with isotopes in different ways (*e.g.* $C_4H_8 + C_4D_8$).

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When using 1-butene as reactant, the decrease of acidic isomerization and increase of metathesis with increasing time of flow was significant but not so decesive as in the case of *cis*-2-butene [8]. This can be explained by the lower reactivity of 1-butene in metathesis and its higher reactivity in acidic isomerization than that of *cis*-2-butene. Another disadvantage arising from the use of 1-butene as reactant is that concomitant with double bond isomerization (Eq. 1) and metathesis (Eq. 2), products of crossmetathesis (Eq. 3) appeared in the reaction mixture.

$$1 - C_4 H_8 \rightleftharpoons 2 - C_4 H_8$$
 (1)

$$2 \ 1 - C_4 H_8 \rightleftharpoons C_2 H_4 + 3 - C_6 H_{12}$$
 (2)

$$1 - C_4 H_8 + 2 - C_4 H_8 \rightleftharpoons C_3 H_5 + 2 - C_5 H_{10}$$
(3)

At higher conversion the metathesis between reactant and product olefins makes the processes more complicated. Despite these difficulties, 1-butene was chosen to test the isomerization and metathesis activity of the catalysts because the composition of the reaction mixture can be determined simply by gas chromatography.

The product distribution obtained over the different catalysts at 373 K vs. time on flow is summarized in Figs 1—4. Over molybdena-alumina (Fig. 1) the rate of isomerization decreased continuously and, consequently, the rate of propene and pentene formation decreased in a similar way. There was only an insignificant change in the concentration of ethene, but that of hexenes increased continuously. At the beginning, the concentration of both pentenes and hexenes was lower than that of the corresponding propene and ethene. Upon approaching the steady state these differences diminished; presumably, they can be accounted for by the greater retention of the higher olefins by the catalyst.

At 373 K the activity of $\text{Re}_2O_7/\text{Al}_2O_3$ was higher in metathesis and lower in isomerization (Fig. 2) than those of molybdena-alumina. The very low concentration of 2-butenes in the reaction mixture was the result of low rate of isomerization and high rate of crossmetathesis. The unusual C_3/C_5 and C_2/C_6 ratios observed at temperatures above 323 K indicate that other side reactions have to be considered. A more detailed study of the processes over rhenia-alumina catalyst is in progress.

Silica supported tungsten catalysts are applied generally in olefin metathesis, little work has been done, however, with tungsten oxide supported on alumina. As can be seen in Fig. 3, this catalyst was effective predominantly in isomerization and had a very low activity in metathesis. The rate of isomerization decreased with the time on flow, but the rate of metathesis, as in the case of molybdena, was more stable.

As has been indicated by OLSTHOORN et al. [5, 6] and by HALL et al. [7, 8], metathesis activity of a given catalyst can be induced by reduction of the transition metal oxides with the reactant olefins. The activity of MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts in metathesis was correlated with their reducibility by THOMAS and MOULIJN [14]. Tungsta-alumina catalysts could be reduced less easily than molybdena-alumina catalysts with the same surface coverage. We supposed that at higher reaction temperatures the WO_3 would be reduced



Fig. 1. Transformation of 1-butene over a MoO_3/Al_2O_3 catalyst at 373 K, atmospheric pressure; feed rate: 1×10^{-2} mol butene s⁻¹ mol_{MOO3} (6.8 × 10⁻⁶ mol butene s⁻¹ g_A⁻¹O₃)



Fig. 2. Transformation of 1-butene over a $\text{Re}_2O_7/\text{Al}_2O_3$ catalyst at 373 K, atmospheric pressure; feed rate: 2×10^{-2} mol butene s⁻¹ mol_{ResO7} (6.8 × 10⁻⁶ mol butene s⁻¹ g_{AlsO3})

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Fig. 3. Transformation of 1-butene over a WO_3/Al_2O_3 catalyst at 373 K, atmospheric pressure; feed rate: 1×10^{-2} mol butene s⁻¹ mol WO_3 (6.8 × 10⁻⁶ mol butene s⁻¹ g_{Al_2O_3})



Fig. 4. Transformation of 1-butene over Al_2O_3 at 373 K, atmospheric pressure; feed rate: 6.8×10^{-6} mol butene s⁻¹ gAl_2O

more deeply, consequently, the metathesis activity would increase more significantly. As will be seen later, at any temperature studied, isomerization remained the prevailing reaction over tungsta-alumina.

For comparison, experiments were carried out over a pure alumina carrier under the same conditions as on supported catalysts. It has to be noted (Fig. 4) that the *cis/trans*-butene ratio in the product formed over alumina varies between 0.7-0.9, while the same ratio over tungsta-alumina is 1.9-2.3,

over molybdena-alumina 2.8—3.7 and over rhenia-alumina only *cis*-2-butene is observable. These values suggest that isomerization on alumina proceeds *via* other routes than on alumina supported transition metal oxides. LOM-BARDO *et al.* [15] presumed that butene isomerization on alumina proceeds *via* formation of an allyl carbanion. Over MoO_3/Al_2O_3 catalysts, however, proton catalyzed isomerization *via* 2-butyl carbenium ion was suggested by HALL *et al.* [9] despite that the observed *cis/trans*-butene ratio was more than unity. Most probably, the same mechanism is effective over WO_3/Al_2O_3 .

During the period of experiments, steady state was not attained, therefore, results at 2 h time on flow were compared to determine the temperature dependence of catalyst activity. Conversions in isomerization, metathesis and crossmetathesis at different temperatures are summarized in Figs 5-7.



Fig. 5. Temperature dependence of the activity of catalysts in isomerization of 1-butene ([2-butenes] + 1/2 [propene] + 1/2 [pentenes])



Fig. 6. Temperature dependence of the activity of catalysts in metathesis of 1-butene ([ethene] + [hexenes])



Fig. 7. Temperature dependence of the concentration of crossmetathesis products formed from 1-butene over the catalysts ([propene] + [pentenes])

Total isomerization conversions were determined as the sum of *cis*- and *trans*-2--butene observed (in %) and the amount of 2-butenes consumed in cross-metathesis as half the sum of propene and pentene (in %).

The isomerization rate increased continuously with raising temperature over each of the catalysts (Fig. 5). The decline of the conversion curve over tungsta-alumina at 373 K is obvious, because the concentration of 2-butenes was close to the equilibrium value. Over rhenia-alumina, isomerization conversions may be higher because of consecutive crossmetathesis.

The tungsta-alumina catalyst was the most active in isomerization at any temperature studied. At temperatures below 350 K the isomerization rate over molybdena-alumina was higher than over alumina, but at higher temperatures the reverse was observed. At temperatures below 400 K, the isomerization rate was unambiguously the lowest over rhenia-alumina.

One has to be careful with the consideration of results at higher conversions; here the product distribution was strongly influenced by the rate of the secondary crossmetathesis. For more precise comparison of the character of catalysts, much more detailed kinetic studies have to be carried out.

The metathesis activity of the catalysts was characterized by the amount of ethene and hexenes (Fig. 6). Over each catalyst, a maximum can be observed in the temperature dependence of the activity. The maximum on rheniaalumina catalyst occurs at 340—350 K, over molybdena-alumina at 430—440 K and approximately at 400 K over tungsta-alumina. The temperature dependence of metathesis activity usually shows such maxima, as reported first by BANKS and BAILEY [16] for $CoO \cdot MoO_3/Al_2O_3$ catalyst.

The concentration maxima of the amount of propene and pentene (Fig. 7) appeared at higher temperatures than those of the metathesis. The
conversion in crossmetathesis is determined by the rate of both metathesis and isomerization. As the isomerization activity increases continuously with temperature, optimal conditions for crossmetathesis are at higher temperatures than for metathesis. Around the maximum, the concentration of crossmetathesis products is much higher than that of the metathesis products under the same conditions. In a mixture of 1-butene and 2-butenes, where the rate of internal metathesis of 2-butenes is higher than the productive metathesis of



Fig. 8. Infrared spectra of pyridine adsorbed on the catalysts; 1. Al_2O_3 ; 2. Re_2O_7/Al_2O_3 ; 3. MoO_3/Al_2O_3 ; 4. WO_3/Al_2O_3



Fig. 9. Infrared spectra of pyridine adsorbed on the catalysts treated previously with 1-butene at room temperature for 20 min; 1. Re₂O₇/Al₂O₃; 2. MoO₃/Al₂O₃; 3. WO₃/Al₂O₃

1-butene [8], according to the reaction scheme given by CASEY et al. [17], predominant formation of the products of crossmetathesis is expected.

At temperatures above 473 K, besides isomerization and metathesis, more or less oligomerization was also observable. Therefore, the temperature dependence of isomerization and metathesis activity was studied only up to 474 K.

The infrared spectrum of pyridine, which is both a Lewis and Brönsted base, has been used successfully to determine the acidity of oxide surfaces. The spectra of pyridine adsorbed on alumina and on alumina supported transition metal oxides can be seen in Fig. 8. The pyridine adsorbed on alumina gave adsorption bands at 1456, 1495, 1574 and 1623 cm⁻¹, which are characteristic for pyridine adsorbed on Lewis acid sites [18]. All bands except those at 1574 cm⁻¹ increased in intensity as compared to alumina. No new band at 1543 cm⁻¹, characteristic for pyridine adsorbed on Brönsted acid sites, appeared. This result is in disagreement with those of KIVIAT and PETRAKIS [18], RATNASAMY and KNÖZINGER [19] and GIL *et al.* [20]; on molydena-alumina, appearance of the Brönsted acid band was observed by them besides an increase of the intensity of Lewis acid bands. The spectra in Fig. 8 do not show any significant differences in the acidity of the three catalysts.

As it was found that the acidity of molybdena-alumina decreased after it was contacted with butenes [7, 8], it can be assumed that the difference in isomerization activity between the three catalysts can be accounted for by the different rates of deactivation by 1-butene. The infrared spectra in Fig. 9 were obtained from adsorbed pyridine on catalysts after 1-butene was adsorbed first. No significant difference in acidity can be recognized even on the basis of these spectra.

Conclusions

1. Over $\text{Re}_2O_7/\text{Al}_2O_3$, $\text{MoO}_3/\text{Al}_2O_3$ and $\text{WO}_3/\text{Al}_2O_3$ catalysts with the same surface coverage at temperatures below 400 K, the rate of double bond isomerization of 1-butene increased and the rate of its metathesis decreased in the above sequence, which is the reverse of that of the reducibility of catalysts. The rate of double bond isomerization over every catalyst increased continuously with increasing temperature, the rate of metathesis followed curves with maxima at different temperatures.

2. Over molybdena-alumina, the selectivity for the formation of $C_2 + C_6$ olefins increased with increasing time on flow; similar increase of selectivity could not be observed over rhenia- and tungsta-alumina catalysts.

3. Brönsted acidity of the catalysts could not be revealed from the infrared spectra of pyridine adsorbed either on fresh or butene treated catalysts; no correlation was found between the isomerization activity of catalysts and the intensity of Lewis acid bands of their spectra.

4. It can be assumed that any catalyst more reducible by the reactant olefin is more active in olefin metathesis and at the same time it has a lower Brönsted acidity. In order to obtain a more exact correlation between metathesis activity, acidity and degree of reduction of the supported transition metal oxide catalysts, more detailed investigations have to be carried out.

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ELECTROCHEMICAL STUDY OF BIMETALLIC CATALYSTS*

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The hydrogen sorption and surface composition of alloys can be investigated by the electrochemical polarization method. The adaptability of this method is demonstrated by the study of dispersed Pd-Hg, Pt-Au/C and Pd-Cu/C catalysts.

The hydrogen sorption characteristics and the calatytic activity of Pd-Hg catalysts strongly depend on the preparation method. In the course of poisoning Hg enriched in the layers near the surface and displaced the strongly bound (adsorbed) hydrogen, whereas Hg influenced mainly the hydrogen dissolved in the bulk of Pd-Hg catalysts prepared by simultaneous reduction.

On the surface of Pt-Au on graphite catalysts Pt enrichment could be observed, which is in connection with the heterogeneities developed during preparation. The change in the surface phase composition of Pd-Cu/C catalysts during aging could be explained similarly.

In order to understand the performance of bimetallic catalysts the knowledge of the surface structure is necessary. The rapidly developing physicochemical methods, especially the spectroscopy methods usually require expensive and complicated equipment. We have chosen the relatively quick and simple electrochemical polarization, which gives information about the surface of the solids.

Galvanostatic and potentiodynamic polarization have been used for characterization of noble metal electrodes for a long time. In this way hydrogen and oxygen sorption and even the surface composition of an alloy can be measured [1]. These polarization methods were adopted for the study of powder catalysts.

Experimental

Analytical grade reagents and distilled water were used in catalyst preparations. The Pd-Hg catalysts containing 0, 7.5, 15.5, 24, 33 and 50 at. % Hg were prepared by simultaneous reduction with NaBH₄. For the preparation of 1 g catalyst, 250 cm³ of a solution containing HgCl₂ and H₂PdCl₄ in adequate amounts and ratio and 200 cm³ 1 wt. % NaBH₄ solution were added dropwise to 200 cm³ H₂O under stirring at room temperature. The catalyst was then filtered, washed with water and dried at 310 K, in vacuum.

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Fig. 1. The electrochemical cell; a – Pt sheet polarizing electrode, b – platinized Pt/H reference electrode, c – catalyst/Pt sheet working electrode

Another series of Hg containing Pd catalysts was prepared by poisoning. Pd catalyst was prepared by hydrogenation in alkaline medium. 100 cm³ 5 wt. % H₂PdCl₄ solution was added to 200 cm³ 7.5% NaHCO₃ solution at 330 K, under stirring. The catalyst was filtered, washed and dried at 330 K, in vacuum. Small portions of this Pd was poisoned by different amounts of HgCl₂ in hydrogen atmosphere for 4 h, while shaking.

The overall metal content of graphite supported Pt-Au catalysts is 10 wt. %. Before use the commercial graphite was activated with concentrated HNO₃ on a steam bath ($S_{BET} = 62 \pm 5 \text{ m}^2 \text{g}^{-1}$). For the preparation of catalysts containing 0, 15, 30, 50, 80 and 100 at. % Au, 0.9 g graphite was impregnated in vacuum with a solution of suitable amounts of HAuCl₄ and H₂PtCl₆. The impregnated, dry support was treated with hydrogen for 30 min at 370 K, washed with water and dried at 340 K.

The Pd–Cu/C catalysts were prepared by consecutive reduction. All the catalysts contained 5 wt. % Pd, while the Cu content was 0, 5, 10, 20, 30 or 40 at. % 47.5 g activated carbon ("Carbo C Extra", $S \approx 1000 \text{ m}^2\text{g}^{-1}$) was impregnated with 350 cm³ 1.7 wt. % H₂PdCl₄ solution. The impregnated support was treated with 5 wt. % NaBH₄ solution, then filtered, washed and dried in vacuum. For the preparation of the Cu containing catalysts, 6 g of 5 wt. % Pd/C was shaken in 100 cm³ water containing the appropriate amount of CuSO₄, in a hydrogen atmosphere. After filtration and washing, the catalyst was dried in vacuum, at room temperature.

The electrochemical cell is shown schematically in Fig. 1. The working and polarizing electrodes were bright Pt sheets, and the reference electrode a platinized Pt/H_2 electrode. A Luggin capillary stretched from the reference electrode to the catalyst powder which was placed on the horizontal Pt working electrode. The three electrodes were separated by ground glass taps. The dry catalyst could be saturated with hydrogen by removing the reference and polarizing electrodes and joining gas lines. After that the cell could be filled with O_2 -free sulfuric acid electrolyte in Ar atmosphere. The anodic polarization started from 10-50 mV. In this way an active catalyst could be measured without pretreatment, in contrast with those procedures when a powder catalyst is rendered measurable by compression or by embedding in some solid, conductive medium.

The activities of the catalysts were studied in the liquid phase hydrogenation of cyclohexene. 20 mg catalyst and 0.002 mol cyclohexene were shaken in 12 cm^3 ethanol at room temperature and atmospheric pressure. The activity was regarded as the initial value of the hydrogen consumption in unit time, referred to 1 g catalyst.

Results and Discussion

In some cases the electrochemical study of hydrogen sorption is of significant help if the change in the activity of the catalysts is to be interpreted. The investigation of Pd-Hg catalysts prepared in two different ways is an example of this.

The potentiodynamic curves of Pd-Hg catalysts prepared by simultaneous reduction are shown in Fig. 2. There are two main hydrogen ionization maxima in the curve of unalloyed Pd. (An additional third peak could be distinguished by applying a lower rate of potential change.) The first, weakly bound



Fig. 2. Potentiodynamic curves of Pd-Hg alloy catalysts prepared by simultaneous reduction (0.5 mol cm⁻³ sulfuric acid, m = 4 mg, v = 10 mV min⁻¹); a – unalloyed Pd, b – 7.5 at. % Hg, c - 15.5 at. % Hg, d - 24 at. % Hg

Hg content, at. %	Hydrogen content (cm ³ g ⁻¹)			Location of maxima in the hydrogen
	weakly bound	strongly bound	total	range, mV
0	42	15	57	63, 185, 260
7.5	29	14	43	70, 260
15.5	11	10	21	80, 257
24.0	_	_	10	
33.0	_	—	4.	
50.0	_	_	. 0	_

Table I

Characteristics of hydrogen sorption on Pd-Hg catalysts prepared by

hydrogen is considered as hydrogen dissolved in the β -phase; the second, strongly bound is attributed to adsorbed hydrogen, according to BURSHTEIN's approximation [2].

The area under the curve is decreased by Hg, *i.e.* the quantity of sorbed hydrogen is lowered (Table I). The decrease is significant at the peak of the weakly bound hydrogen. From 24 at.% Hg the two types of hydrogen cannot be separated, for the energetic distribution of sorbed hydrogen became almost uniform. Hydrogen sorption ceased at 50 at.%.

The potentials belonging to the hydrogen ionization maxima were also determined: the rate of potential change was decreased until the position of the peak did not change any more, and the approximate value of ohmic potential drop was taken into account [3].

On the unalloyed Pd catalyst three kinds of hydrogen are sorbed (Table I). The first maximum corresponding to dissolved hydrogen shifted from 63 mV



Fig. 3. Identity distances of Pd-Hg alloy catalysts as a function of composition



Fig. 4. Potentiodynamic curves of Pd catalysts poisoned by mercury, in 0.5 mol dm⁻³ sulfuric acid (m = 4 mg, v = 10 mV min⁻¹); a – unpoisoned Pd, b – 5 at. % overall Hg content, c – 17.5 at. % overall Hg content

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to 80 mV upon the action of Hg, *i.e.* the energy of metal-hydrogen bond increased. The bond energy of the strongly bound, mainly adsorbed hydrogen virtually did not change. (Curves shown in Fig. 2 were not recorded at this "limiting rate".)

Consequently, Hg influences mainly the hydrogen dissolved in the bulk of the Pd-Hg catalysts prepared by simultaneous reduction. X-ray diffraction measurements support this fact (Fig. 3). The identity distance of Pd incresses linearly with Hg content. In the course of preparation, Hg continuously alloyed into the Pd lattice, while expanding it.

The potentiodynamic curves of Pd catalysts poisoned by Hg show other characteristics (Fig. 4). As a result of poisoning, the quantity of strongly bound hydrogen decreases primarily. From an overall Hg content of 17.5 at.% on, only weakly bound, mainly dissolved hydrogen can be seen. Another important difference is that the bond energy of dissolved hydrogen does not change between 0 and 33 at.% of overall Hg content: 62-65 mV in each case.

In the course of poisoning, Hg is concentrated in the surface layers and displaces the strongly bound (adsorbed) hydrogen. However, Hg deposited on the surface is partly alloyed with the Pd, and because of it, the amount of dissolved hydrogen decreases, too.

The X-ray diffraction peak of Pd was not shifted with increasing Hg content, but it was broadened asymmetrically towards the smaller angles (higher lattice constant). This is consistent with the picture obtained in hydrogen sorption investigations: the poisoned catalysts contain predominantly unchanged Pd; asymmetric broadening is caused by the various Hg-containing surface layers.

On the basis of the above facts the difference between the activity of the two types of catalysts can be understood (Fig. 5). Hg poisoning caused a rapid decrease in activity, whereas the alloy catalysts of low Hg content are



Fig. 5. Relative activity of Pd-Hg catalysts prepared by simultaneous reduction (1) and by poisoning with Hg (2), in the hydrogenation of cyclohexene

more active than the Pd itself. On alloying the activity ceases at higher Hg content than in poisoning.

The determination of the surface composition of an alloy is shown on the example of graphite supported Pt-Au catalysts. The two extremities are in Fig. 6, the voltammograms of the catalysts containing only Pt or Au besides graphite. The location of the cathodic oxygen desorption peak is about 0.7 V for Pt and about 1.2 V for Au. Hydrogen is sorbed on Pt only.

The curves of the alloy catalysts can be regarded as a sum of the two curves, if there are Pt-rich and Au-rich phases present on the surface [4]. The curve of the catalyst containing 30 at.% Au and prepared by consecutive hydrogenation is shown in Fig. 7. The surface area of the phases can be determined from the area under the curve: that of Pt from the hydrogen sorption, that of Au from oxygen desorption [1]. The curve of the suitable amount of graphite support has to be taken off as the background.

The most important characteristics of the catalysts prepared by simultaneous reduction are given in Fig. 8 as a function of Au content related to the overall metal content. It can be seen that the surfaces of the catalysts containing 15 and 30 at.% Au are homogeneous, and Au appears as a new phase only at 50 at.% However, the surface Au/Pt ratio even then is significantly below the bulk ratio. The result was the same if the catalysts were prepared not with hydrogen, but with NaBH₄ or HCOH. Only the catalysts prepared by consecutive reduction were exceptions. Thus on the surface of



Fig. 6. Potentiodynamic curves of Pt/graphite (1) and Au/graphite (2) catalysts in 0.5 mol dm^{-3} sulfuric acid (m = 10 mg, v = 100 mV min⁻¹)



Fig. 7. Potentiodynamic curves of 10 mg 30 at. % Au - 70 at. % Pt/graphite catalyst prepared by consecutive reduction (1) and 9 mg graphite support (2) in 0.5 mol dm⁻³ sulfuric acid (v = 100 mV min⁻¹)



Fig. 8. Surface Au concentration (Au_s) , dispersity (D) and activity (A) of Pt-Au/graphite catalysts as a function of overall Au concentration (Au_0)

the graphite supported Pt-Au catalysts prepared by simultaneous reduction, Pt enrichment can be observed. The reason of it is that the entering of Au into the new solid phase is always quicker than that of Pt.

The change in dispersity is not significant in the range of low gold content; the decrease becomes sharp above 50 at.%.

The activity in the hydrogenation of cyclohexene increases until the surface of the catalyst is homogeneous (up to 30 at.%). Then it decreases quickly

in accordance with the decrease of dispersity and the increase of surface Au/Pt ratio.

On the basis of the results it can be assumed that a homogeneous alloy was formed on the surface of the catalysts during preparation. The surface Au concentration increases with the overall Au concentration, but it is always smaller than the latter. The surroundings of the active centers are changed by the Au present in a few % and the change in activity is due mainly to this ligand effect. These conclusions are in contradiction with the views in the literature that the surface of Pt-Au alloys is always heterogeneous and Au can be regarded simply as a diluting component [1, 5].

Our third example is about the investigation of Pd–Cu catalysts on activated carbon support. In this case a part of the phenomena observed during aging could be interpreted by the potentiodynamic curves.

In the curve of the catalyst of 5 at.% Cu proceeding in the anodic direction, after the two hydrogen ionization maxima, two further peaks can be seen after preparation (Fig. 9, curve *a*). The peak around 340 mV can be attributed to the anodic dissolution of metallic Cu. The peak around 540 mV can be interpreted assuming that not Cu-Cu, but Cu-Pd bonds are broken. (That is why there is a 200 mV potential shift.) This maximum can be attributed to the dissolution of some Pd-Cu intermetallic compound phase [6].

One month later the copper disappeared from the surface and the amount of compound phase decreased. At the same time hydrogen sorption and the catalytic activity also changed. Similar results were observed on the investigation of the catalysts containing less than 30 at.% Cu. The catalysts were stabilized only 4 months after preparation. (These catalysts were stored in air closed double.)

It may be established that upon consecutive reduction, Cu deposited in hydrogen atmosphere is alloyed with the Pd on carbon. The mobility of metal atoms in the surface layers of the catalysts is so high that the penetration of Cu atoms into the lattice of Pd continued during storage at room temperature.

According to the "bond-breaking" segregation theory, in hydrogen atmosphere, the surface of the Pd-Cu alloy is poor in Cu, for the chemisorption heat of hydrogen is substantially higher on Pd [8, 9]. Thus Cu is easily alloyed with Pd in the course of preparation. The situation is the reverse in air; Cu is the more volatile component and the chemisorption heat of oxygen is higher on Cu, too [10-13]. The process during aging tended to the contrary of the expected direction.

The explanation is that the segregation theories worked out for alloys in equilibrium do not say much about the surface composition if the catalyst is prepared at relatively low temperatures, in our case below 400 K. The difference of the surface and bulk composition of the catalyst prepared in this way is determined by the following factors:

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Fig. 9. Potentiodynamic curves of 5 at. % Cu–Pd/C catalyst (a) 0.5 month, (b) 1.5 months, (c) 2.5 months and (d) 4 months after preparation



Fig. 10. Surface and bulk composition of A-B alloy; 1 – concentration of component B in equilibrium, 2 and 3 – surface enrichment of components A or B, respectively, during preparation

- 1) The heterogeneity occurring during preparation (e.g. consecutive reduction, or the slow entering of one of the components into the solid phase, which results in a situation similar to consecutive reduction). The difference between the characteristics of Pd-Hg catalysts prepared in two ways and the development of the surface composition of graphite supported Pt-Au catalysts were interpreted in this way, too.
- 2) Stabilization processes taking place in the course of aging during the time from the preparation till the utilization.

In both cases the presence of support, the particle size and the chemical nature of the surrounding atmosphere can play an important role.

The surface and bulk compositions of an alloy catalyst prepared at relatively low temperature are compared with the expectable equilibrium values in Fig. 10. The *B* component of the *A*—*B* alloy has the lower surface energy. From kinetic reasons either the *A* or the *B* component can be enriched on the surface of the particles during preparation. (The probability that equilibrium according to the given particle size is reached, is very small.) In the case of surface enrichment of the *B* component, x_B will decrease on the surface during storage. Thus, apparently, the direction of migration is contrary to that expected on the basis of segregation theory, provided that the process takes place at the given temperature. The driving force of the process is the free enthalpy decrease of mixing.

The latter case corresponds to the process taking place on carbon supported Pd-Cu catalysts. The fact that migration of the Cu atoms from the surface layers (from where it may dissolve in the course of anodic polarization) towards the inside of the grains took place observably can be connected with the high dispersity of the catalysts and with the "irregularity" of the grains.

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HYDROGEN ADSORPTION ON Cu-Ni ALLOY CATALYSTS*

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Hydrogen adsorption isotherms have been measured on two Cu-Ni bulk alloys (5 at. % and 30 at. % Cu) in a wide range of pressure $(5 \times 10^{-5} \le P \le 5 \text{ Torr})$ and of temperature (190 K $\le T \le 460$ K).

For both alloy compositions, the isotherms are of the TEMKIN type. The isosteric adsorption heat Q decreases from an initial value of *ca*. 20 kcal for the 5 at. % Cu alloy and *ca*. 12 kcal for the 30% Cu alloy, to a value around 7 kcal, identical for both alloys at close to monolayer coverage. The ratio of the H₂ monolayer value to the 77 K Kr BET monolayer is = 0.63, identical, within experimental error, for both alloys.

It is concluded that hydrogen adsorption cannot be used to "titrate" surface Ni atoms and that the adsorption site is composed of mixed ensembles of Cu and Ni atoms in varying proportion following coverage.

Introduction

Ni-Cu alloy is one of the most extensively studied bimetallic catalysts as it is often considered as a model system for alloy catalysis. Dilution of Ni, a very active metal for chemisorption of most gases as well as for the catalysis of numerous reactions, by Cu, which is known to be inactive in many similar situations, leads to effects in chemisorption and catalysis that have been classified into two main groups [1]:

- *ligand effects*, related to changes in the adsorbate-active metal bond strength due to changes in its surroundings

- geometric or ensemble effects, due to variations in the distribution of the available ensembles of active metal atoms.

Whichever the expected ligand or ensemble effect, the interpretation of experimental results requires the knowledge of the surface concentration of active metal. Here a complication arises from the well known Cu surface enrichment of low dispersity Cu-Ni catalysts.

Determinations of the surface Ni concentration have been carried out by several methods.

i. Theoretical calculations that clearly demonstrated the surface enrich-

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ment [2, 3]. These theoretical calculations are based on experimental values of several parameters (surface free energy, surface entropy) the values of which are sometimes known with a large error only. As a consequence, calculated values of surface composition can only be considered as correct within an order of magnitude.

ii. Surface science methods, mainly Auger electron spectroscopy [5, 6]. These methods are mainly applied to single crystal surfaces, and in the case of Cu-Ni mainly to the 110 face. As this face is less dense than the 100 and 111 ones, it may represent but a small percentage of the surface of real catalysts. Furthermore, methods of cleaning of the surface in surface science studies, by ion bombardment for example, are very different from the chemical methods used with real catalysts. Thus, conclusions drawn from surface science studies may not be valid for real catalysts.

iii. Selective hydrogen chemisorption. On pure Ni, at room temperature at not too low pressures (P > 0.1 Torr), it is usually assumed that the hydrogen coverage is close to the monolayer. Under the same conditions, pure Cu does not adsorb hydrogen. In the selective hydrogen chemisorption hypothesis, it is assumed that the properties of the individual Ni and Cu atoms are not modified by alloving, so that in the alloy the chemisorption sites are Ni atoms that can be "titrated" by bydrogen adsorption. In this hypothesis, it is in fact assumed that for H_2 chemisorption, there is neither a ligand effect nor an ensemble effect. Absence of ligand effects is based on theoretical calculations of the density of states, as well as on experimental measurements of this density. These measurements have been interpreted in the following manner: when an adsorbate interacts with electrons of a certain energy level, it can be known with high certainty whether these electrons originate from Ni or from Cu [1]. But the absence of ensemble effects did not receive any clear justification. On the contrary, theoretical calculations have shown that ensemble effects could account for the variation of the adsorption heat with alloying [15], and recent results of H₂ thermodesorption from 110 single crystal faces of Cu-Ni alloys have led to the tentative explanation that sites constituted by mixed Cu-Ni ensembles do adsorb hydrogen [16, 17].

The present work has been undertaken mainly to verify if the selective chemisorption hypothesis is valid. Hydrogen sorption isotherms measured in a wide range of temperature and pressure will allow to determine the H_2 monolayer value as well as the thermodynamic parameters characterizing H_2 adsorption. These measurements will be carried out on a series of alloys in the whole range of composition from pure Ni to pure Cu, as well as on both pure metals. To facilitate comparison with previously published results, unsupported alloys of low dispersity prepared following the manner already used by SINFELT *et al.* [8] in their well known work on ethane hydrogenolysis and cyclohexane dehydrogenation will be used.

The present paper reports results obtained on two alloys widely differing in composition: 5 at.% and 30 at.% in Cu, that should correspond, following published results, to widely differing Ni surface concentrations, in the range of 50-60% for 5% Cu alloy and around 15% for the 30% Cu alloy [7, 8].

Study of the other compositions is in progress.

Experimental

Apparatus and procedures

Apparatus and procedures for measuring the adsorption isotherms and the thermodesorption spectra have been described in a preceding paper [10].

Catalysts

The bulk copper-nickel alloys were prepared following the method described previously by a number of workers [8, 9, 11–13]: precipitation of the metals as carbonates, calcination in air at 400 °C to convert the carbonates to the mixed oxides and reduction in H_2 at 400 °C. The reduction was conducted following the procedure described in [8]. The extent of reduction, always higher than 99%, was controlled gravimetrically and the composition of the alloys was checked after reduction by dissolving a small sample of catalyst and weighing the metals separately deposited electrolytically on a Pt electrode. The catalysts stored and bottled in air were, before use in adsorption measurements, reduced again *in situ* in flowing H_2 (30 cm³ STP min⁻¹) at 400 °C for 8 h, then outgassed at 300 °C (residual pressure in the 10^{-7} Torr range) for 15 h.

Results

General

The specific surface area of both alloys was measured by Kr adsorption at 77 K in the pressure range where multilayer adsorption takes place and thus the BET equation is valid ($0.03 \le P \le 0.6$). Respective values of Kr monolayer m(Kr) are:

 $(6.4 \pm 0.1) \times 10^{18}$ molecules/g for Cu–Ni (5% Cu)

 $(11.0 \pm 0.1) \times 10^{18}$ molecules/g for Cu–Ni (30% Cu)

For nearly equal bulk composition, SINFELT et al. [8] found by Ar adsorption at 77 K (BET method), monolayer values of the same order of magnitude; furthermore, the ratio of Ar (SINFELT) and Kr (this work) monolayers corresponding to both alloys are nearly equal.

All the following measurements were performed on only one sample of each alloy, but periodic checks show that the surface area did not vary in the course of the experiments and thus that the outgassing or reduction treatments did not cause any significant sintering of the powder. This is not surprising as the low dispersity measured indicates that both alloys are already highly sintered.

As a general agreement upon Kr adsorption cross section has not been reached, the Kr monolayer value will not be converted into surface area. But

it is known from the literature that for Ni the ratio of H_2 chemisorption monolayer to Kr monolayer is around 1.25 [14]. Let us note that, for most transition metals, this ratio is between 1 and 1.4 [24]. In order to allow an easier comparison either between both alloys or between each alloy and a somewhat theoretical pure Ni surface, most of the following results will be presented as relative coverage Θ_R values with

$$\Theta_{\mathrm{R}} = rac{n_{\mathrm{a}}}{1.25 \, \mathrm{m(Kr)}}$$

where n_a is the number of adsorbed hydrogen molecules.

In a manner quite similar to what has been reported in the literature on pure Ni surfaces, on both alloys a phenomenon known as "slow chemisorption" is observed: when introducing H_2 in the presence of the catalyst, most of the adsorption takes place before the first pressure measurement (t = 1 min) but then a slow decay of the pressure is observed over a period of more than 1 h at room temperature, somewhat shorter at higher temperatures, until an equilibrium is reached. The amount adsorbed during the slow process, is almost independent of the temperature:

 $(2.5 \pm 0.5) imes 10^{17}$ molecules $m H_2/g$ for 5% Cu alloy

 $(4.5 \pm 0.5) \times 10^{17}$ molecules H₂/g for 30% Cu alloy.

In the case of pure Ni surface, a common explanation of this well known slow chemisorption is the contamination of the surface by oxygen, either due to insufficient reduction of the catalyst and migration of O atoms from bulk to surface in the presence of H_2 , or contamination by residual vacuum pressure (H_2O) during outgassing [18, 19]. Other possible explanations are H_2 absorption in the bulk of the metal [20] or surface migration of H_2 to less accessible sites [14]. In the case of an alloy such as Ni–Cu, where it is admitted that H_2 adsorption takes place mainly on Ni and where surface enrichment in Cu does exist [2, 5], a further explanation may be proposed: chemical pumping of Ni atoms from bulk to surface by H_2 ; as a result, the surface becomes richer in Ni as compared with this surface under vacuum. Such phenomena have already been observed on Pt–Sn alloys [21].

In an attempt to obtain more information on these possible processes, the following experiment was performed: the Ni-Cu alloy was heated under H₂ pressure at 300 °C for several hours, then rapidly cooled under H₂ at 175 °C and outgassed at this temperature (in place of the normal outgassing temperature of 300 °C). From a rough extrapolation of measured isotherms (see below), one would expect the residual H₂ coverage Θ after outgassing at 175 °C to be less than 0.03, *i.e.* almost negligible. As the solid state diffusion is much slower at 175 °C than at 300 °C, one would also expect either a higher Ni surface concentration (due to chemical pumping of Ni after heating under H₂ at 300 °C)

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or a lower surface O_2 content (due either to complementary reduction before low temperature outgassing or to slower diffusion). In fact, isotherm measurement performed after such outgassing procedures do not show any significant differences from isotherms measured after "normal" outgassing, concerning both the total adsorbed amount and the slow adsorption process. Thus, surface contamination by oxygen does not appear as a correct explanation of the slow chemisorption and chemical pumping of Ni does not take place in Ni–Cu alloys.

Another fact worth mentioning is the "activated" adsorption observed at low temperatures (T < 190 K): larger adsorbed amounts are observed at low temperatures when introducing H₂ at room temperature (or higher), then cooling the catalyst at the adsorption temperature, than upon introducing H₂ directly at the adsorption temperature. This fact is common to H₂ adsorption on metallic catalysts [10, 14, 20].

Another "activated" adsorption phenomenon is observed when heating - the alloy at temperatures higher than 200 °C under H_2 pressure, then cooling the catalyst at a lower temperature; the adsorbed amount so measured is always higher than upon introducing H_2 directly at the adsorption temperature.

All the desorption isotherms reported in the following were measured after introduction of H_2 at the adsorption temperature and after having allowed slow chemisorption to proceed until no significant pressure variation is measured.



Fig. 1. H_2 adsorption isotherms on two Cu–Ni alloys: (a) 5% Cu alloy: (1) T = 193 K, (2) T = 293 K, (3) T = 361 K, (4) T = 417 K, (5) T = 462 K; (b) 30% Cu alloy: (1) T = 193 K, (2) T = 248 K, (3) T = 293 K, (4) T = 364 K, (5) T = 441 K

Desorption isotherms

Desorption isotherms were measured at pressures between $\simeq 5 \times 10^{-5}$ Torr and $\simeq 10$ Torr, in the temperature range of 193—460 K for both alloys. Results are presented in Fig. 1. The variation with coverage of the isosteric heat of adsorption Q and of the corresponding adsorption entropy ΔS , which can be deduced from these isotherms by application of Clapeyron's equation, are given in Figs 2 and 3.



Fig. 2. Variation of the heat of H₂ adsorption Q with relative coverage Θ_R on two Cu–Ni alloys: (1) 5% Cu alloy; (2) 30% Cu alloy



Fig. 3. Variation of entropy of H₂ adsorption ΔS with relative coverage Θ_R on two Cu–Ni alloys: (1) 5% Cu alloy; (2) 30% Cu alloy



Fig. 4. Compensation effect between heat Q and entropy $\varDelta S$ of ${\rm H_2}$ adsorption on 5% Cu–Ni alloy

Apparently, except at very high (low temperature, high pressure) or very low (low pressure, high temperature) coverages, the coverage varies almost linearly with the logarithm of the pressure, thus corresponding to TEM-KIN's isotherm, whose derivation is based on a linear variation of Q with Θ , in good agreement with the results of Fig. 2. Furthermore, a compensation effect between adsorption heat and adsorption entropy is observed (Fig. 4) for the 5% Cu alloy. For the 30% alloy, adsorption entropy is almost independent of the adsorption heat.

Monolayer coverages $V_{\rm m}$ have been determined by applying the Langmuir adsorption equation to the high pressure part of the 193 K isotherm, implicitly admitting that near full coverage, in a restricted range of coverage, the adsorption heat does not vary and thus Langmuir's equation may be applied. The following values are found:

for 5% Cu alloy: $V_{\rm m}=4.1 imes10^{18}$ molecules ${
m H}_2/{
m g},$ i.e. $\Theta_{
m R}=0.51$

for 30% Cu alloy: $V_{\rm m}=6.9 imes10^{18}$ molecules ${
m H_2/g},$ i.e. $\Theta_{
m R}=0.50.$

Both values of $V_{\rm m}$ are also in agreement to within 0.1×10^{18} molecules ${
m H_2/g}$ with the adsorbed amount at 77 K under $\simeq 1$ Torr ${
m H_2}$.

Thermodesorption spectrum

Figure 5 illustrates a few TDS spectra measured at adsorption desorption equilibrium with a heating rate around 40 K min⁻¹ on both alloys at different coverages. At all coverages, only one peak is observed. This peak appears rather symmetrical, except at low Θ_R (< 0.05) where tailing on the high temperature side is observed. The temperature of peak maximum does not depend



Fig. 5. Thermal desorption spectrum of H₂ for different initial coverages: (a) 5% Cu-Ni alloy, (1) $\Theta_{\rm R} = 0.439$; (2) $\Theta_{\rm R} = 0.112$; (b) 30% Cu-Ni alloy, (1) $\Theta_{\rm R} = 0.428$; (2) $\Theta_{\rm R} = 0.102$

on coverage for $\Theta_{\rm R} > 0.15$: 410 K (±10) for 5% Cu alloy, 425 K (±10) for 30% alloy, this difference in the temperature of peak maximum for both alloys being not significant. At lower coverages ($\Theta_{\rm R} < 0.150$) the temperature of peak maximum increases: up to 455 K for 5% Cu alloy ($\Theta_{\rm R} = 0.11$), up to 535 K for 30% Cu alloy ($\Theta_{\rm R} = 0.045$). At $\simeq 600$ K, for both alloys, the whole of H₂ absorbed at low temperatures is desorbed. Let us recall here that the temperatures mentioned here were measured at the outside of the bulb containing the catalyst; real temperature in the catalysts is certainly several tens of K lower. As the location of the temperature differences at peak maximum between both alloys are not significant.

Discussion

As presented in the introduction, previous work on Cu-Ni alloys emphasized two main points:

— surface enrichment in Cu [1-6];

- possible titration of surface nickel atoms by hydrogen chemisorption considered as selective, *i.e.* taking place exclusively or at least mainly on Ni atoms [1].

The following Table gives the surface concentration of Ni for both alloys used in the present study, as determined by:

- Auger electron spectroscopy (AES) [5];

- selective hydrogen chemisorption (SHC) [7-8];
- theoretical calculations [2-4].

Let us note that the value by SHC of Ref. [7] was obtained using the adsorbed amount of H₂ at 293 K at a pressure in the 5×10^{-2} Torr range. However, the value of Ref. [8] was obtained at 293 K, using the so-called distinction between "reversible" and "irreversible" adsorptions so that the measured adsorbed amount must correspond to an equilibrium pressure equal to the pressure existing above the catalyst at the end of a pumping stage; this may be estimated to be in the 10^{-3} — 10^{-4} Torr range. In both cases, the adsorbed amount that is supposed to correspond stoichiometrically to Ni surface atoms, is measured on one particular isotherm, the 293 K one, chosen arbitrarily, at one particular pressure $\sim 5 \times 10^{-2}$ Torr in one case, $\sim 10^{-3}$ — 10^{-4} Torr in the other, also chosen arbitrarily, without any justification.

The selective chemisorption hypothesis can now be considered in the light of the results obtained in the present study. If, as usually admitted, only or mainly chemisorption takes place on Ni, the completion of the monolayer on Ni must correspond to a sharp break in the thermodynamic parameters characterizing the H_2 adsorption. No such break is observed, either in the adsorption heat, or the entropy of adsorption. On the contrary, one observes a smooth decrease of the adsorption heat with increasing coverage: for the entropy, variation is also smooth but following the alloy, an increase or decrease is observed. Thus, our results do not support the selective chemisorption hypothesis. On the contrary they support a model where adsorption takes place

Method	AES [5]	SHC [8]	SHC [7]	Theoretical [4]
95% Ni	$\simeq 80^+$	$\simeq 40$	$\simeq 65^+$	40 - 60
70% Ni	$\simeq 40$	$\simeq 20$	$\simeq 14$	10 - 20

Surface concentration of Ni (%)

 $^{+}$ = Value deduced by interpolation from published curves.

on ensembles of Ni and Cu atoms; rich in Ni at low coverage and progressively richer in Cu as coverage increases, in very good agreement with theoretical models [15]. It is interesting to note that the adsorption heat at low coverage is higher on the 5% Cu alloy where ensembles richer in Ni must exist, but at progressively higher coverages, adsorption taking place on ensembles poorer in Ni, the adsorption heat becomes equal on both alloys. That is the reason why the H₂ monolayer values are in first approximation equal on both catalysts. Other recent studies of H₂ adsorption on 110 single crystal faces of Cu–Ni alloys have also been interpreted in terms of ensembles [16, 17].

The amounts of adsorbed H_2 , assumed to correspond stoichiometrically to Ni surface atoms, were measured in Refs. [7] and [8] under temperature and pressure conditions chosen arbitrarily, as shown above. The H_2 monolayer values determined in the present paper are not arbitrary values but characteristic properties of the alloys studied. Unfortunately, in the frame of an interpretation by ensembles, the monolayer value is not simply related to the Ni surface concentration as it depends upon the unknown distribution function of Ni atoms in the ensembles defining the chemisorption sites. That is the reason why approximately equal values of the monolayer are obtained on two alloys widely different in bulk composition and certainly also in surface composition. Nevertheless, it allows to conclude that the surface of both alloys is enriched in Cu, but this point is not confirmed on low dispersity Cu–Ni alloys.

It is possible that more unambiguous conclusions on surface composition and distribution function in the ensembles could be drawn from entropy data.



Fig. 6. Entropy of hydrogen adsorbed on two Cu-Ni alloys: (1) 5% Cu-Ni alloy; (2) 30%. Cu-Ni alloy. Comparison with theoretical models: Curve 1: Translational entropy (ideal gas); Curve 2: Translational entropy (VOLMER model)

Entropy of H in the adsorbed phase as a function of coverage is given for both alloys in Fig. 6. Important differences do appear as the entropy is slowly decreasing with coverage on 30% Cu alloy, whereas an inverse variation is observed on 5% Cu alloy. The variation of the translational entropy with coverage, calculated for a two-dimensional gas, either ideal or non-ideal (Volmer model) [22], is also represented in Fig. 6. As the rotational contribution to the entropy unit [23], the translational entropy is equal, in first approximation, to the total entropy. Agreement between calculated and experimental values is satisfactory for 30% Cu alloy. But for 5% Cu alloy, no model of adsorption, either mobile or immobile (configurational entropy), can account for the experimental values. Probably, a systematic—investigation of several alloys with differet compositions should throw some light on this problem.

As concerns the TDS results, the most surprising fact is the existence of a unique peak of desorption as one should expect the surface of an alloy to be highly heterogeneous with respect to H₂ adsorption. H₂ measurements on a 110 single crystal indeed show three peaks, attributed to pure Ni sites, to mixed Ni–Cu sites and to pure Cu sites [16, 17]. But this result may be particular to the 110 face where atoms in the second layer just beneath the surface are partly apparent. As the 110 face is less dense than the 111 and 100 faces, it may represent but a very small fraction of the total surface in the bulk alloys used in this study. Thus, from the TDS results, it again appears that H₂ adsorption takes place on mixed ensembles of Cu–Ni atoms, whose composition varies slowly with coverage, with the possible exception of very low coverages ($\Theta_{\rm R} < 0.05$).

The adsorption heat Q may also be derived from TDS using the relation valid for dissociative adsorption and TDS spectra measured at equilibrium:

$$Q = rac{RT_{
m m}^2}{eta} \; rac{F \, P_{
m m}}{n_{\infty}} \; rac{2}{artheta_{
m m}(1 - artheta_{
m m})}$$

where $T_{\rm m}$, $\Theta_{\rm m}$, $P_{\rm m}$ are, respectively, temperature, pressure and coverage at peak maximum, F the pumping speed, n_{∞} the amount adsorbed at full coverage (expressed in the same units as the product $FP_{\rm m}$) and β the heating rate. The Q values derived in this manner are in agreement, within experimental error, with the values of Fig. 2, derived from the isotherms.

Conclusions

Study of H_2 adsorption on two Cu–Ni alloys widely differing in composition has shown that:

— the H_2 monolayer values per unit surface are equal;

- the adsorption heat decreases slowly with increasing coverage: the initial heat is higher on low Cu alloys, but the heats at high coverage are equal on both alloys.

These facts do not support the model of selective chemisorption of H₂ on Ni atoms or pure Ni ensembles at the surface of the alloy and thus H_a adsorption does not allow to measure the surface Ni concentration.

More information will certainly be deduced from an extensive study now in progress on a series of Cu-Ni alloys of variable composition.

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HYDROGENOLYSIS OF ETHANE AND EXCHANGE WITH D₂ ON RHODIUM DURING THE BUILD-UP OF HYDROCARBON COVERAGE*

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The isotope exchange and hydrogenolysis of C_2H_6 with D_2 on evaporated Rh films were measured in a flow reactor during the build-up of hydrocarbon coverage and during displacement from the surface of chemisorbed hydrocarbon residues. The gaseous composition was continuously determined by mass spectrometry. The adsorption rate of light ethane, the rate of desorption of adsorbed C_2 radicals by the mechanisms of both single exchange and multiple exchange, the hydrogenolysis rate and the hydrocarbon coverage C_S were simultaneously measured. The value of C_S is determined from the integrated in-out total mass balance.

It is shown that all chemisorbed hydrocarbon radicals (C_S) are reversibly chemisorbed and that the rate of methane formation is always simply proportional to the amount of C_S . On the contrary, the rate of single exchange is independent of C_S but is simply proportional to the adsorption rate of ethane.

During the build-up, an increase of activity for multiple exchange is observed together with an increase of activity for hydrogenolysis. During the displacement, it is concluded that ethane is formed from chemisorbed C_1 radicals, thus the breaking of the C-C bond is reversible. It is also concluded that, in spite of the small hydrocarbon coverage (less than 2%), the rate limiting step of hydrogenolysis is methane desorption and that the most abundant surface intermediate is a C_1 radical. An analysis of the results obtained by the method used here allows to determine also the rates of surface steps such as the breaking of the C-C bond.

Introduction

In the study of catalysts, the hydrogenolysis reaction of ethane has been used extensively as a test reaction owing to its very large demanding properties and its structure sensitivity [1–12]. On the other hand, it appears that the mechanism of that reaction is still under discussion and it is not clear which step is responsible for the demanding aspect and structure sensitivity.

It is not reasonable to assume the same mechanism and furthermore the same step being rate-determining on all catalysts, as made for example in the extensive work of SINFELT.

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The multiple bonding of the various radicals resulting from the dissociative chemisorption of ethane has been proposed to be the reason for the structure sensitivity [1-12].

We have analyzed the effect of H_2 pressure and hydrogen coverage on the adsorption step of alkanes [13].

It appears that the active site for alkane chemisorption is composed of a large ensemble of H chemisorption sites and that there is competition for adsorption between hydrogen and the alkane. The adsorption rate of the alkane is thus strongly dependent on the hydrogen coverage that appears in the rate equation as $(1 - \Theta_{\rm H})^{Z}$, where Z is the number of H chemisorption sites defining the active site for alkane chemisorption. As a result, the adsorption step presents a demanding character [14] and the surface coverage function contains an important compensation effect [15].

It has been shown [16] that the adsorption step of ethane on rhodium films obey the same mechanism whatever happens to the adsorbed radical, exchange with D_2 or hydrogenolysis.

On the other hand, we have previously shown in the study of CH_4-D_2 exchange that it is possible to find experimental conditions such that the composition of radicals chemisorbed on the metal surface may reach equilibrium in 10^2 to 10^3 s [17]. It is then also possible in a flow system to derive the coverage from the integrated value of the in-out mass balance.

In the work presented here, we have measured the hydrogenolysis of ethane and the exchange with D_2 on evaporated rhodium films during the build-up in hydrocarbon coverage as well as during the cleaning of the surface of hydrocarbon residues with hydrogen. The use of hydrogen in the form of D_2 allows to distinguish an ethane molecule that has never been adsorbed from an ethane molecule that has been adsorbed, and will thus appear in the gas phase as one of the deuterated isomers of ethane. We can thus measure simultaneously the adsorption rate of light ethane (R_a) , the desorption rate of adsorbed C_2 species following simple exchange (R_S) and multiple exchange (R_{ME}) mechanism, the hydrogenolysis rate (R_A) and the total hydrocarbon surface coverage (C_S) at any moment during the transient period necessary for the surface composition, the activity and the selectivity of the catalyst to reach steady values.

Experimental

The reaction vessel, of UHV type, was build from "Varian" parts, the bulb in which the film is evaporated was of Pyrex glass (Fig. 1). The procedure of film preparation has already been described [16].

Deuterium is allowed to flow in the reaction vessel with the reaction bulb at reaction temperature (liquid thermostat) until an adsorption-desorption equilibrium is attained. The reaction bulb is then isolated by closing valve 3.

The alkane is then introduced under flow conditions in the "by pass" until steady flow conditions are attained. The opening of valve 3 represents time zero of a "build-up" experiment.

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Fig. 1. Schematic diagram of the UHV reaction vessel

The "cleaning" of the surface from hydrocarbon residues starts upon turning of the inlet valve 2 for the hydrocarbon. All the flow is entering the mass spectrometer. The flow is of molecular type owing to the pressure range. Thus the introduction of a second component (alkane) in the gas flow does not modify the partial pressure or the volumic flow rate of the first component (D_2) . Furthermore, the diffusion rate, which is equal to the conductance of the vessel, is about 10^{2} Ls⁻¹ for D₂, whereas the volume flow rates used in the vessel are 2.500 cm³. The main residence times range from about 15 to 250 s. These rates were calculated by use of the following equation:

$$R_i = (\Phi_{\rm in})_i - (\Phi_{\rm out})_i + \frac{N_{\rm a}V}{RT} \cdot \frac{\mathrm{d}p_i}{\mathrm{d}t}$$
(1)

where Φ_{in} and Φ_{out} are the molecular flow in and out the reaction vessel (in molec. s⁻¹), V is the volume of the reaction vessel and p_i is the partial pressure of gas *i*. The time constant necessary to obtain a signal in the mass spectrometer proportional to the pressure is of the order of a few seconds.

Reactants

Catalyst: evaporated Rh film under UHV conditions ($p < 10^{-9}$ Torr), Rh filament from Johnson-Matthey (99.9% purity) C₂H₆ from "L'Air Liquide" (99.95% purity) D₂ from "L'Air Liquide" (isotopic purity better than 99.6%), purified by diffusion

through a Pd-Ag thimble. Analysis of the gas composition was performed continuously by mass spectrometry (Varian GD 150).

Results

Two experiments will be analyzed here, conducted at 50 °C and a deuterium pressure of 4.3×10^{-3} Torr. The volume flow rate for D₂ was 88.9 cm³ s⁻¹. The first experiment (Rh 1882) corresponds to a "build-up" in hydrocarbon coverage until steady conditions of catalytic activity are attained, whereas the second one (Rh 1883) corresponds to a "cleaning" of the surface in chemisorbed hydrocarbon residues. Figures 2 and 3 show how the partial pressures of the different species in the gas phase vary with time during these two experiments. Under the conditions used here it takes more than an hour to reach steady catalytic activity. Furthermore, multiple exchange and hydrogenolysis produce only perdeuterated ethane and methane, with account of the isotopic dilution in the deuterium gas that in these experiments remains constant at $P/(P + D) = 9.7 \times 10^{-3}$ in Rh 1882 and of 4.3×10^{-3} in Rh 1883.

For Rh 1882, the value of the various rates ($R_{\rm a}$ = adsorption rate of light ethane C_2P_6 , $R_{\rm SE}$ rate of single exchange, $R_{\rm ME}$ rate of multiple exchange in ethane molecules per second and $R_{\rm H}$ rate of hydrogenolysis in methane molecules per second) calculated using Eq. (1) are plotted against time in Fig. 5, together with the hydrocarbon content of the surface expressed as the number of carbon atoms $C_{\rm g}$. These results show that the selectivity for hydrogenolysis, multiple exchange and single exchange vary strongly during the



Fig. 2. Rh 1882: Variation of the different partial pressures with time. Curve 1: pressure of CD_4 in 2×10^{-5} Torr, curve 2: pressure of C_2P_6 in 1×10^{-4} Torr, curve 3: pressure of C_2P_5D in 5×10^{-6} Torr, curve 4: pressure of C_2D_6 in 1×10^{-5} Torr



Fig. 3. Rh 1883: Variation of the different partial pressures with time. Curve 1: pressure of CD_4 in 2×10^{-5} Torr, curve 2: pressure of C_2P_6 in 5×10^{-5} Torr, curve 3: pressure of C_2P_5D in 5×10^{-6} Torr, curve 4: pressure of C_2D_6 1×10^{-5} Torr



Fig. 4. Rh 1882: Build-up in hydrocarbon coverage. Curve 1: instant carbon mass balance on the surface in 2×10^{13} atoms s⁻¹, curve 2: total chemisorbed hydrocarbon residues in 5×10^{16} carbon atoms



Fig. 5. Rh 1882: Variations of the rates of adsorption (R_a) , hydrogenolysis (R_H) , single exchange (R_{SE}) and multiple exchange (R_{ME}) together with the variations in hydrocarbon coverage (C_S) with time. Curve 1: R_H in 2×10^{13} molec. sec⁻¹, curve 2: R_a in 5×10^{13} molec. sec⁻¹, curve 3: R_{SE} in 5×10^{12} molec. sec⁻¹, curve 4: R_{ME} in 1×10^{13} molec. sec⁻¹, curve 5: C_S in 5×10^{16} atoms

build-up in hydrocarbon coverage. The hydrocarbon coverage is derived from the total in-out mass balance (Fig. 4) on the surface. The coverage in hydrocarbon residues, expressed as the number of carbon atoms $C_{\rm S}$, reaches a value of $2.8 \times 10^{16} C_{\rm S}$, as compared to the number of chemisorption sites measured by H₂ chemisorption of 1.8×10^{18} H sites. In other words, the hydrocarbon coverage at steady conditions is still very small. The rate of single exchange is always proportional to the adsorption rate of light ethane, independently of

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the value of $C_{\rm S}$. The increase of activity for multiple exchange should be described by two time constants, different by a factor larger than 100. The larger of these two time constants is equivalent to the one characterizing the variation of $R_{\rm H}$ as well as the variation of $C_{\rm S}$. It can also be seen that the rate of methane formation is always nearly proportional to $C_{\rm S}$. In experiment Rh 1883, this proportionality is valid (Fig. 6), whereas in both experiments there is no simple relation between $R_{\rm ME}$ and $C_{\rm S}$.

Figure 7 shows that in Rh 1883, the partial pressure of light ethane decreases exponentially with time with a time constant of about 60 s. Let us remember here that the volume flow rate of light ethane out of the reaction ves-



Fig. 6. Rh 1883: Cleaning of the surface in C_1 and C_2 species. Curve 1: R_H/C_S in 1×10^{-3} molec. s⁻¹ $C_{\overline{S}}^{-1}$, curve 2: R_{ME}/C_S in 2×10^{-4} molec. s⁻¹ $C_{\overline{S}}^{-1}$, curve 3: C_S in 5×10^{16} atoms



Fig. 7. Rh 1883: Exponential decay of the pressure in C_2P_6 (curve 1: 5×10^{-5} Torr), of R_{SE} (curve 2 in 2×10^{12} molec. s⁻¹) and of R_{ME} (curve 3 in 1×10^{13} molec. s⁻¹) with time

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Fig. 8. Rh 1883: Decay of $R_{\rm H}$ (curve 1 in 2×10^{13} molec. s⁻¹), of $R_{\rm ME}$ (curve 2 in 1×10^{13} molec. s⁻¹) and of $C_{\rm S}$ (curve 3 in 5×10^{16} atoms)

sel is 32.5 cm³ s⁻¹ and the volume flow rate equivalent to the adsorption rate at steady conditions is 11.5 cm³ s⁻¹. The volume of the reaction vessel being of 2570 cm³, the calculated time constant for the decrease of the pressure of C_2D_6 is about 59 s. This result allows to conclude that in the whole pressure range covered in Rh 1883, the adsorption rate is always first order in $P_{C_2P_4}$.

One also sees in Fig. 7 that the rate of single exchange is always proportional to $P_{C_zP_s}$ and thus to R_a . The rate of multiple exchange behaves in a completely different way. When plotting log R_{ME} versus time (Fig. 8), it appears that the decrease of R_{ME} during the cleaning in hydrocarbon residues is characterized by two time constants. On the other hand, the same Figure shows that the decrease of R_H and C_S is characterized by the same time constant, 1.25×10^3 s, which is close to the inverse of the probability of desorption of a carbon atom from the surface, R_H/C_S (Fig. 6).

Discussion

The simple proportionality of R_{SE} to R_a is in agreement with a reaction scheme previously proposed for the adsorption of methane and ethane [16]. This scheme, corresponding to a reactive type mechanism, is

$$(C_2H_6)_g + (H)_a + ZS \stackrel{(1)}{\rightleftharpoons} (C_2H_7)_a \stackrel{(2)}{\rightleftharpoons} (C_2H_5)_a + (H_2)_g$$
(2)

Under the conditions used here, viz. a large excess of gaseous D_2 and very fast exchange between the gaseous deuterium and the pool of chemisorbed hydrogen atoms, (H_a) must be a deuterium atom. The reverse reaction of step 1

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(decomposition of the complex $(C_2H_7)_a$ may only give rise to single exchange but as it expresses the probability for an adsorbed C_2H_6 molecule in the form of the association complex $(C_2H_7)_S$ to undergo chemisorption or desorption, as long as the hydrocarbon coverage remains small, the ratio of these probabilities will not be affected by variations in C_S .

As during the build-up in $C_{\rm S}$ as well as during the cleaning of the surface in $C_{\rm S}$, $R_{\rm H}/C_{\rm S}$ is always about constant and close to the inverse of the time constant characterizing the decrease of $R_{\rm H}$ and $C_{\rm S}$ (Fig. 6), the product of hydrogenolysis must be a C_1 radical. The variation of R_{ME} in two steps in both experiments would suggest the existence of two types of sites, one inducing only exchange with a short time constant for the surface to adapt to that species. The other one induces both exchange and hydrogenolysis, the rate of which would vary with a time constant in the range of 10³ s. An important objection to that interpretation is that R_{SE} is independent of C_S and simply proportional to $R_{\rm a}$. Thus only one type of site should give rise to single exchange! Anyway, this could be explained by chemisorption on site 1 through a reactive adsorption mechanism and chemisorption on site 2 through a dissociative mechanism. This is in contradiction with previous results concerning $R_{\rm a}$ [16], where it has been shown that the adsorption of ethane proceeds through the same mechanism under conditions of both exchange and hydrogenolysis.

It is important to note here that during the slow decrease in $R_{\rm ME}$ (second part of decrease of $R_{\rm ME}$ in Fig. 8) the value of $R_{\rm ME}$ is always proportional to the square of $R_{\rm H}$ (Fig. 9). The surface being mainly composed of C_1 radicals, this is experimental proof that the breaking of the C—C bond on the surface is a reversible step. Furthermore, since the amount of C_2 radicals on the sur-



Fig. 9. Rh 1883: $R_{\rm ME}$ versus $R_{\rm H}$ during the cleaning of the surface in C_1 and C_2 species

face is small as compared to the C_1 radicals, whereas the rate of ME is of the same order of magnitude as the rate of hydrogenolysis, the probability of desorption of a C_2 radical is much larger than that of a C_1 radical. Thus, the square dependence of $R_{\rm ME}$ on $R_{\rm H}$ must be related to the kinetics of the reverse step of C—C bond breaking and not to the equilibrium of that step.

Thus we now may consider the following reaction scheme:

$$(C_{2}H_{6})_{g} \stackrel{(1)}{\longleftrightarrow} (C_{2}H_{7})_{a} \stackrel{(2)}{\longleftrightarrow} \dots (C_{2}H_{x})_{a} \stackrel{(3)}{\longleftrightarrow} \dots (C_{1}H_{y})_{a} \stackrel{(4)}{\longleftrightarrow} \dots (CH_{4})_{g}$$
$$\Theta_{C_{4}} \qquad \Theta_{C_{1}} \qquad (3)$$

where all C_2H_x are in equilibrium with each other and all C_1H_y are also in equilibrium with each oter. Step 4 is considered as always out of equilibrium because we know [16] that under the experimental conditions used here the readsorption of CH_4 may be completely neglected. Let us now analyze the results in the frame of Eq. (3):

$$d\Theta_{C_2}/dt = R_2 + R'_3 - R'_2 - R_3$$
(4)

and

$$\mathrm{d}\Theta_{\mathrm{C}_{1}}/\mathrm{d}t = R_{3} - R_{3}' - R_{4}. \tag{5}$$

It is interesting to note that

$$R_2 = R_{\rm a} - R_{\rm SE} \tag{6}$$

$$R_2' = R_{\rm ME} \tag{7}$$

$$R_{\rm H} = R_4 \tag{8}$$

In the first part of Fig. 5, $C_{\rm S}$ is negligible and R'_3 must thus also be negligible. But if $R_{\rm ME}$, which must be proportional to $\Theta_{\rm C_3}$, reaches a steady value, we may write that

$$\begin{aligned} \frac{\mathrm{d}\Theta_{\mathrm{C}_2}}{\mathrm{d}t} &\simeq 0\\ S_0(R_3)_1 &= (R_2)_1 - (R_2')_1 = (R_\mathrm{a})_1 - (R_\mathrm{SE})_1 - (R_\mathrm{ME})_1 \\ &= (1.90 - 0.22 - 0.32) \times 10^{13} = 1.36 \times 10^{13} \text{ molec. s}^{-1}. \end{aligned} \tag{9}$$

In the above general scheme, it is logical to suppose that

$$R'_2 \alpha \Theta_{C_a}$$
 and $R_3 \alpha \Theta_{C_a}$ (10)

Thus R_3 should vary as $R'_2 = R_{ME}$.

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and

We may now calculate the value of R_3 under steady conditions (end of Fig. 4) and as again

$$\frac{\mathrm{d}\Theta_{\mathrm{C}_2}}{\mathrm{d}t} \simeq 0$$

$$R_3 = 1.36 \times 10\ 10^{13}\ \frac{5.7 \times 10^{12}}{3.2 \times 10^{12}} = 2.42 \times 10^{13} \text{ molec. s}^{-1}$$

$$R_2 = 1.70 \times 10^{13} - 0.19 \times 10^{13} = 1.51 \times 10^{13} \text{ molec. s}^{-1}$$

$$R'_2 = 5.7 \times 10^{12} \text{ molec. s}^{-1}$$

$$R'_3 = 2.42 \times 10^{13} + 5.7 \times 10^{12} - 1.51 \times 10^{13} = 1.48 \times 10^{13} \text{ molec. s}^{-1}$$

As in the final part of Fig. 8, we measure in fact the rate of step 3', the extrapolation of $R_{\rm ME}$, to t = 0 in Fig. 8 corresponding to R'_3 , gives the value of R'_3 under steady-state conditions (end of Rh 1882). This value is about 2.2×10^{12} molec. s⁻¹, in disagreement with the value of 1.48×10^{13} calculated above.

Thus the scheme expressed by Eq. (3) is too simple. On the other hand, it is also difficult to reconcile the value of the time constant characterizing the first fast decrease of $R_{\rm ME}$ (Fig. 8), which is about 200 s, with the time constant characterizing the first fast increase of $R_{\rm ME}$ (Fig. 5), which is less than about 10 s.

We therefore propose a scheme as follows:

$$(C_{2}H_{6})_{g} \xrightarrow{(1)} (C_{2}H_{7})_{a} \xrightarrow{(2)} (C_{2}H_{x})_{a} \xrightarrow{(3)} (C_{2}H_{y})_{a} \xrightarrow{(4)} (C_{1}H_{z}) \dots \xrightarrow{(5)} (CH_{4})_{g}$$
$$\Theta_{C_{2}}' \qquad \Theta_{C_{1}}' \qquad (11)$$

where none of the C_2 radicals are in equilibrium with each other. C_2H_x and C_2H_y may than correspond to different degrees of dehydrogenation or may also correspond to different positions of the same radicals on the surface, if they are mobile.

It follows that the values of R_2 , R_3 , R'_2 and R'_3 are the same as the one calculated above. But now, the rate of 2.2×10^{12} molec. s⁻¹ (extrapolation of $R_{\rm ME}$ to $R_{\rm ME} t = 0$ in Fig. 8) gives the value of R'_4 in

$$\frac{\mathrm{d}\Theta_{\rm C_1}}{\mathrm{d}t} = R_4 - R_4' - R_5, \quad \text{with} \ R_5 = R_{\rm H}. \tag{12}$$

We then calculate for steady-state conditions:

$$R_4 = R_5 + R_4' = 2.2 imes 10^{12} + 9.0 imes 10^{12} = 1.12 imes 10^{13}$$
 molec. sec⁻¹.

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The rate constant of step 2' in this scheme is larger than the rate constant of step 3' and $\Theta_{\rm C} > \Theta_{\rm C}$. This explains the large difference in the values of the time constants characterizing the first fast increase of $R_{\rm ME}$ (Fig. 5) or characterizing the first fast decrease of $R_{\rm ME}$ (Fig. 8).

As a conclusion, the transient method used here together with the use of D_{2} provides simultaneously extensive information on the various rates (R_{a}, R_{SF} , $R_{\rm ME}, R_{\rm H}$) and on the hydrocarbon coverage during the period where the surface composition is adapting to the gas phase. This body of information gives an insight into surface steps that is not available from conventional kinetic studies.

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INFRARED STUDY OF CHEMISORBED BENZENE ON SILICA SUPPORTED NICKEL*

(SHORT COMMUNICATION)

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Studies of benzene adsorption have been performed by Fourier Transform Infrared Spectroscopy on a Ni/SiO₂ catalyst at room temperature.

The infrared spectra were measured on Digilab FTS-14 and a Digilab FTS-20 infrared interferometers. The infrared cell, the method of sample preparation and experimental technique have been described elsewhere [1].

A specially prepared disc pressed from the impregnated silica sample allowed to record the spectra below 1300 cm⁻¹ down to 600 cm⁻¹. The comparison of the infrared and Raman [2] spectra leads to the first spectroscopic evidence of $C_{6\nu}$ symmetry group for adsorbed benzene on Ni. More than 25 bands of chemisorbed benzene were detected and a weak vibrational coupling between neighbouring benzene molecules was observed, too.

Part of the adsorbed benzene at low coverage is chemisorbed with loss of its aromatic character. The formation of C_4 species was found on hydrogen-"rich" surfaces, while on hydrogen-"poor" surfaces, C_6 species was formed during chemosorption. The comparison of vibrational data for chemisorbed benzene and condensed Ni with C_6H_6 at low temperature (~ 10 K) [3] and the organometallic π -cemplexes of $M(C_6H_6)_2$ [4] showed that the benzene ring perturbation is similar and weak in the first two cases but much stronger for sandwich molecules.

All our observations are in good agreement with the results of High Resolution Electron Energy loss spectroscopy on Ni(100) and (111) single crystal faces [5] with the exception of the umbrella (v_{11}) vibration. More detailed results will be published very soon.

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CYCLIZATION OF C₇-ALKANES OVER Pt BLACK CATALYST*

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 C_{6} - and C_{5} -cyclization of heptane isomers (and also, olefin formation as a related process) over Pt-black have been studied in pulse and circulation systems. Hydrogen-deficient conditions favour aromatization, via presumably terminal olefins. C_{5} -Cyclization in the presence of more hydrogen is accompanied by internal olefin formation. Relative reactivities of all heptane isomers have been measured: this shows that cyclization is easier between terminal methyl groups. Optimum hydrogen pressures for both types of cyclization have been determined (and compared with hydrogenolysis, too). Earlier mechanism suggestions for aromatization and cyclopentane formation have been confirmed; the distinction between two types of bond shift mechanisms producing aromatics (from substituted pentanes) and saturated isomers, respectively, has received additional support facilitating the identification of these two reactions with mechanisms proposed in the literature.

Introduction

Several parallel reactions may occur when alkanes are reacted over Pt catalysts. It has been shown that the selectivity of catalysts is greatly influenced by the presence of hydrogen: in helium, aromatization (and some olefin formation) are the main products, whereas C_5 -cyclic alkanes and skeletal isomers also appear in hydrogen [1]. The yields of these reactions have maxima as a function of hydrogen partial pressure; this was shown in both pulse [2] and static-circulation reactors [3]. A hypothesis has been put forward that the position of the maxima as a function of the hydrogen pressure would be characteristic of the degree of dissociation of the surface intermediate for the given reaction [4]. This hypothesis may be related to the more exact formulation of reactive adsorption by FRENNET et al. [5] who claimed that Z "potential adsorption sites" should interact with the molecule (in addition to the single "landing site"). These sites are, as a rule, occupied by hydrogen; thus the hydrogen coverage appears in the expression of the reaction rate in the Z-th power (Z being generally a high number). This results in rather steep hydrogen dependencies.

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Aromatization would require the most dissociated surface intermediates. This would correspond to the stepwise aromatization mechanism involving surface alkenes, alkadienes and alkatrienes as intermediates [6, 7]. The aromatization of substituted pentanes takes place via dehydro-isomerization, involving similarly or still more dissociated surface intermediates [8]. This, presumably bond shift type reaction differs from the process producing saturated isomers [9]. Hydrogenolysis also requires multiply dissociated intermediates but because the reaction requires stoichiometric hydrogen uptake, the maximum yield lies at higher hydrogen pressures [9]. C₅-Cyclic reactions (ring opening and closure as well as C₅-cyclic isomerization) require less dissociated surface species. As opposed to literature suggestions [10] a flat lying half-hydrogenated intermediate was suggested for it [11], whereby the cyclization step would resemble the associative complex suggested by LIBER-MAN [12].

Olefins would be by-products of cyclization. A hydrogen-rich environment favourable for C_5 -cyclic ractions would produce internal olefins while mostly terminal olefins have been found under hydrogen-deficient conditions [11]. This could be explained by the different types of adsorption under these two conditions [13].

In order to collect chemical evidence for the above-mentioned reactions, it is reasonable to aim at the study of as many isomers as possible. Thus, the common features can be collected and the individual features may give information as far as the correlations between reactivity and molecular structure are concerned. Heptane isomers were selected for the present work, because they undergo rather easily all reactions enumerated and they do not result in so numerous products which would render evaluation intolerably difficult.

The present work will deal with the cyclization reactions of heptane isomers (paying particular attention to their hydrogen dependence) and, also related isomerization processes will be tackled. Hydrogenolysis will form a separate publication.

Experimental

Apparatus

A CHROM 31 type gas chromatograph served for analysis of the reaction products. Two types of reactors could be joined to it alternatively: a pulse-type microreactor [14] or a static-circulation reactor of 160 cm³ volume [15] from which 1 cm³ gas samples could be introduced by means of a six-way sampling valve. Samples were introduced in the liquid state into the microreactior using a syringe and a rubber septum. The analysis was carried out using a 50 m steel capillary column wetted by squalane.

Catalyst

Pt-black was reduced from aqueous solution of H_2PtCl_6 by HCHO in the presence of KOH [16]. It was pretreated at 633 K in H_2 for 1 hour; the H_2 was introduced after heating up the catalyst in air. This type of treatment has reportedly produced the largest crystallites

[17]. The specific surface of this Pt-black after sintering was about 2 m^2/g (BET, N₂), its average crystallite size: about 30 nm. The catalyst was regenerated at the temperature of the measurement by the oxygen of air, followed by hydrogen treatment. This treatment was claimed to be able to restore catalytic activity [18]. Since, however, the total activity of the catalyst decreased somewhat from one day to another, its actual activity level was checked by standard *n*-heptane experiments. The results have been corrected with respect to the daily activity level.

Hydrocarbons

n-Heptane (*n*-Hp), 2-methylhexane (2-MHx), 3-methylhexane (3-MHx), 3-ethylpentane (3-EP), 2,3-dimethylpentane (2,3-DMP), 2,4-dimethylpentane (2,4-DMP) and 2,2,3-trimethylbutane (2,2,3-TMB) were gas chromatographic standards supplied by MERCK. 2,2-Dimethylpentane (2,2-DMP) and 3,3-dimethylpentane (3,3-DMP) were "purum" grade FLUKA reagents. Their gas chromatographic purity corresponded to the $\geq 99.5\%$ purity claimed by the suppliers. The hydrocarbons were used without further purification; when they were filled into the storage vessels of the circulation apparatus, they were de-aerated by triple freeze-thaw cycles.

Carrier gases were purified by a deoxygenating column and dried. Hydrogen to the circulation apparatus was fed through a palladium thimble.

Evaluation

Peak areas were hand calculated using the response factors taken from the literature [19]. Reaction rates could be substituted by conversion values taken in the 5th minute.

Results

Selectivity of heptane isomer conversions in hydrogen and helium

The effect of helium or hydrogen on the selectivities has been studied in pulse system. Table I gives summarized data on selectivities observed in helium. Here, apart from extensive fragmentation, mostly aromatization and

Table I

Selectivity of transformations of heptane isomers (He carrier gas, pulse system, $T=663~{
m K}$)

Starting C ₇ H ₁₈	Conversion	Selectivity (%)					
	(mol%)	< C,	Toluene	Benzene	Olefin		
<i>n</i> -Hp	0.50	60.3	6.0	23.8	9.8		
2-MHx	0.76	45.6	17.5	28.0	8.8		
3-MHx	0.88	60.3	7.2	27.4	5.0		
3-EP	0.75	59.6	1.8	22.9	15.7		
2,3-DMP	0.56	56.9	1.9	18.7	22.4		
2,4-DMP	0.27	64.3	13.7	22.1	a		
2,2-DMP	1.26	83.2	4.5	4.8	7.5		
3,3-DMP	0.67	71.5	3.8	7.9	16.8		
2,2,3 - TMB	0.87	88.4	1.1	a	10.5		
		1	1				

* Not separated from the reactant

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Starting	Conversion	Selectivity (%)						
$C_{7}H_{16}$	(mol%)	$< C_7$	Aromatics	Olefin	C5-cyclic	Isomer	Other ^a	
n-Hp	0.40	17.0	4.0	62.7	11.0	5.3	_	
2-MHx	0.81	14.3	14.8	20.1	41.6	4.9	4.3	
3-MHx	0.76	11.8	7.1	63.4	15.8	1.3	0.6	
3-EP	1.36	12.3	-	57.8	26.4	3.5		
2,3-DMP	0.70	4.3	_	72.6	22.6	0.4	_	
2,4-DMP	0.86	13.7	_	b	76.3	3.5	6.5	
2,2-DMP	0.28	11.0	-	50.4	38.6	-	_	
3,3-DMP	0.08	37.4	-	62.6	-	-	-	
2,2,3-TMB	0.22	50.0	-	50.0		-	_	

Selectivity of transformations of heptane isomers (H₂ carrier gas, pulse system, T = 663 K)

^a Not identified products

^b Not separated from the reactant

olefin formation predominates. It must be noted that a considerable part of aromatics appeared as benzene. Olefin formation selectivities are also relatively high. Because of the large number of possible positional double bond isomers, in some cases (e.g. with 2-methylhexane, 2,4-dimethylpentane) some of them might have overlapped with the peak of unreacted hydrocarbons, thus higher olefin selectivities (e.g. in the case of 3-ethylpentane or 2,3-dimethylpentane) could rather be regarded as typical. Nevertheless, the transformation of olefins to aromatics [18] is more typical under these conditions.

In hydrogen, aromatization and hydrogenolysis are both suppressed. Apart from the expected appearance of C_5 -cyclic products and isomers, the high olefin formation selectivity should be pointed out (Table II). The composition of the olefins changes in a way predicted on the basis of experiments with 3-methylpentane. [11]. Typical results are shown in Table III.

Effect of molecular structure on the reaction directions

Tables I and II have already shown that the selectivities depend strongly on the molecular structure. If conversions are referred to a selected standard compound (*n*-heptane seemed most reasonable), a clear picture can be obtained. Table IV demonstrates that the cracking of nongeminal isomers are close to each other, tertiary C atoms being somewhat more reactive. Quaternary C atoms increase the fragmentation tendency several times. Aromatization of 2-methylhexane takes place with maximum yields. This may be due to statistical effects: the two terminal methyl groups increase the probability of 1,6-

ring closure by a factor of 2. It should be noted that substituted pentanes gave only slightly less aromatics than *n*-heptane. Even 2,2,3-trimethylbutane gave a small amount of aromatic products. Olefin formation from each isoheptane was higher than that from *n*-heptane. Neither the higher fragmentation nor the higher olefin formation of hydrocarbons with quaternary C atom was observed in hydrogen (Table V). Larger differences were observed in aromatization activity: in hydrogen, methylhexanes formed most aromatics while aromatization requiring skeletal rearrangement could not be observed at all.

Effect of hydrogen pressure on catalytic selectivity

No comparison at a single hydrogen pressure could give reliable results on the relative reactivity of various heptane isomers. This was investigated in the circulation system, changing the hydrogen pressure with fixed hydrocarbon pressure. Results are shown in Figs 1—9 for all heptane isomers studied.

Conversion to olefins (mol%) in		Product olefin	Selectivity of individual olefins (%) in		
Не Н ₂	H ₂		He	${\rm H_2}$	
0.262	0.858		100	10.2	
			_	89.8	
0.261	0.517	\downarrow	18.3	3.0	
			56.3	31.2	
			25.4	8.8	
		-	_	57.0	
	0.261	Conversion to olefins (mol%) in He H ₂ 0.262 0.858 0.261 0.517	Conversion to olefins (mol%) in Product olefin He H_a 0.262 0.858 0.261 0.517 0.261 0.517	Conversion to olefins (mol%) in Product olefin Selectivity o olefins He Ha He 0.262 0.858 \checkmark 100 \checkmark \checkmark $-$ 0.261 0.517 \downarrow \downarrow \downarrow $ 0.261$ 0.517 \downarrow \downarrow \downarrow $ 0.261$ 0.517 \downarrow \downarrow \downarrow $-$	

Table III

Structure of olefinic products in helium and hydrogen (pulse system, T = 663 K)

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Starting	onversion to olefins (mol%) in		Product olefin	Selectivity of olefins (f individual %) in
C ₇ H ₁₆	He H ₂	H_2		He	${\rm H_2}$
3-MHx	0.101	0.513		100	-
				_	4.3
				_	28.1
			~	_	17.0
				_	50.6
2,2-DMP 0.303	0.148	\times	64.4	21.2	
			\times	35.6	78.8

Table III (continued)

Table IV

Relative conversions of heptane isomers related to normal heptane (pulse system, He carrier gas, T=663 K)

Starting C ₇ H ₁₀	< C ₇	Aromatics	Olefin
n-Hp	1.0	1.0	1.0
2-MHx	1.1	2.3	0.9
3-MHx	1.0	1.3	0.7
3-EP	1.3	1.1	1.8
2,3-DMP	1.3	0.8	2.0
2,4-DMP	0.5	0.7	a
2,2-DMP	6.1	0.7	2.3
3,3-DMP	2.3	0.7	2.3
2,2,3-TMB	3.6	0.1	2.4

^a Not separated from the reactant

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Table V

Starting C ₇ H ₁₆	< C ₇	Aromatics	Olefin	C ₅ -cyclic	Isomers
n-Hp	1.0	1.0	1.0	1.0	1.0
2-MHx	1.1	5.5	0.7	2.5	1.2
3-MHx	1.1	3.6	2.1	1.6	0.4
3-EP	2.2	-	1.4	7.5	3.1
2,3-DMP	0.5	_	1.7	1.9	0.2
2,4-DMP	0.9	-	a	4.8	1.0
2,2-DMP	0.5		0.6	2.1	_
3,3-DMP	0.8	_	0.3	_	_
2,2,3-TMB	0.9		0.7	-	-

Relative conversions of heptane isomers related to normal heptane (pulse system, H_2 carrier gas, T = 663 K)

^a Not separated from the reactant

The yields of most products have maxima as a function of the hydrogen pressure. As a general conclusion, it can be stated that the partial pressure at the maxima depends on the adsorption strength of the reactant hydrocarbon. This "strength" may correspond to the degree of dissociation of the surface intermediate in question and this is as follows:



This order is more or less the same as proposed previously for Pt [4] and Pd [9] catalysts. One conspicuous exception is that bond shift isomerization was put at the end of the sequence since it has its (very flat) maximum at highest hydrogen pressures. It was impossible to determine the exact maximum for bond shift isomerization with hexanes as reactants: with heptanes, however, some processes (e.g. 2-methylhexane from *n*-heptane or the reverse reaction) could have occurred via a bond shift mechanism only.

Whereas the sequence of the maxima depended on the type of the reaction and the structure of the reactant played a secondary role in it, the actual reaction rates (heights, and sometimes also the position of the maxima) depended strongly on the structure of the hydrocarbon (Figs 1—9).



Fig. 1. Rates of transformation of n-heptane as a function of the hydrogen pressure (staticcirculation system, hydrocarbon pressure 1.23 kPa, T = 603 K)



Fig. 2. Rates of transformation of 2-methylhexane as a function of the hydrogen pressure (conditions: see Fig. 1)

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Fig. 3. Rates of transformation of 3-methylhexane as a function of the hydrogen pressure (conditions: see Fig. 1)



Fig. 4. Rates of transformation of 3-ethylpentane as a function of the hydrogen pressure (conditions: see Fig. 1)

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Fig. 5. Rates of transformation of 2,2-dimethylpentane as a function of the hydrogen pressure (conditions: see Fig. 1)



Fig. 6. Rates of transformation of 2,4-dimethylpentane as a function of the hydrogen pressure (conditions: see Fig. 1)

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Fig. 7. Rates of transformation of 2,2-dimethylpentane as a function of the hydrogen pressure (conditions: see Fig. 1)



Fig. 8. Rates of transformation of 3,3-dimethylpentane as a function of the hydrogen pressure (conditions: see Fig. 1)

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Fig. 9. Rates of transformation of 2,2,3-trimethylbutane as a function of the hydrogen pressure (conditions: see Fig. 1)

Kinetic parameters

The pulse system permitted us to determine apparent activation energy values taking the (usually low) conversion proportional to the reaction rate. The results (together with analogous literature data [8]) have been compiled

Table	VI
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Apparent activation energy for the aromatization of hexanes and heptanes (pulse system, He carrier gas, calculated from the total aromatic yield)

Prestant	E_{a} , kJ/mol				
Reactant	Present study	Literature data [8,20]			
<i>n</i> -Hp	45	<i>n</i> -Hx	42		
2-MHx	31				
3-MHx	34				
3-EP	78	2-MP	75		
2,3-DMP	71	3-MP	71		
2,4 - DMP	64	2,3-DMB	84		
2,2-DMP	67	2,2-DMB	84		
ECP	85	МСР	75		

in Table VI. The higher energy barrier of aromatization of substituted pentanes is obvious; no large differences can be seen between hexanes and heptanes in this respect.

In the presence of hydrogen, higher energies of activation have been reported [20]. Thus, it can be expected that the $E_{\rm a}$ values for aromatization measured in the presence of hydrogen (i.e. in circulation apparatus) will be higher than those reported in Table VI. A complication arises here that — with all the maximum type curves shown in Figs 1-9 — rate values taken at arbitrary hydrogen pressures could easily correspond to different hydrogen orders. A reasonable suggestion was [3] to relate the $E_{\rm a}$ values to the maximum yields where the reaction order with respect to hydrogen is zero. As the temperature increases, the maxima are shifted to higher and higher hydrogen pressures as demonstrated by Fig. 10. This means that at higher temperatures a higher hydrogen pressure is necessary to maintain the same — obviously optimum — hydrogen coverage. The apparent energy of activation values determined in the way shown above may correspond therefore to constant and optimum hydrogen coverages. The E_a value determined for *n*-heptane aromatization on the basis of Fig. 10a is 136 kJ mol⁻¹. This can be compared with the value of 226 kJ mol⁻¹ recalculated on the basis of Ref. [20] for n-hexane over Pt-black in hydrogen of constant 1 bar pressure, using a pulse system. Here 2-methylpentane gave the same $E_{\rm a}$ value, indicating that rearrangement is no longer rate-determining in H2. A similar result has been ob-



Fig. 10. Rates of toluene (a), ethylcyclopentane (b) and 2-methylhexane (c) formation from n-heptane as a function of the hydrogen pressure at 583 K (1), 603 K (2) and 633 K (3) (staticcirculation system, hydrocarbon pressure 1.23 kPa)

tained in the present study for 2-methylhexane ($E_{\rm a}$ for aromatization in hydrogen: 244 kJ mol⁻¹). Since the C₅-cyclic reactions require higher hydrogen coverage and this absolute value cannot be always maintained at higher temperature (no maximum is reached at 633 K in Fig. 10b) no exact calculation was possible for these processes.

Discussion

The above facts are in accordance with previous suggestions about reaction routes and mechanisms and also give additional information. As far as *aromatization* is concerned, the results are in agreement with the stepwise dehydrocyclization of hydrocarbons (alkane \rightarrow olefin \rightarrow diene \rightarrow triene) with at least 6 carbon atoms in their main chain [4, 6, 7]. A new observation is that the rate of cyclization decreases if a methyl group is attached to the carbon chain: Fig. 11 demonstrates the following order of reaction rates:



Aromatization is often accompanied by rearrangement of the molecule. Two such reaction types occur here: one involves aromatization of alkanes with 5 or 4 C atoms in their chain. This process has been shown to occur via bond shift type dehydroisomerization [8]. The same mechanism, requiring very dissociated surface intermediates, should be valid with heptane isomers. too. This mechanism should be able to aromatize even 2,2,3-trimethylbutane (Table I). This reaction was attributed to a McKervey-Rooney-Samman type [21] bond shift rearrangement mechanism [9]. The attractive feature of this process was that it could explain the reactivity of quaternary carbon atoms, too. Saturated isomers were interpreted in Ref. [9] by the metalacyclobutane intermediate of GARIN and GAULT [22]. Later, however, GAULT and AMIR-EBRAHIMI described the metalacycloalkane mechanism as one involving surface carbenes [23]. Such species can be formed under hydrogendeficient conditions and should be responsible for the recently recognized homologation reactions [24-26] occurring also on Pt, at high temperature and lower hydrogen pressures. Therefore, we attribute now the dehydroisomerization to a metalacyclobutane type dehydroisomerization involving surface carbenes as intermediates. These rearranged surface species form aromatics with low surface hydrogen coverages like it was proposed by SÁRKÁNY and TÉTÉNYI [25]:



 C_6 -dehydrocyclization



Fig. 11. Rates of aromatization of n-hexane and various heptane isomers as a function of the hydrogen pressure (conditions: see Fig. 1; 1: n-Hx, 2: 2-MHx, 3: 3-MHx, 4: n-Hp, 5: 3-EP, 6: 2,4-DMP, 7: 2,2,3-TMB)

Table VII

Ratio of the aromatization products from heptane isomers (as a function of the temperature, pulse system)

a) He carrier gas

$\begin{array}{c} {\rm Starting} \\ {\rm C_7H_{16}} \end{array}$	Benzene/toluene at T (K)							
	603	633	648	663	678	693		
n-Hp	_	0.97	1.27	1.79	2.00	2.58		
2-MHx	0.51	1.28	1.44	1.63	1.91	2.03		
3-MHx	0.79	2.05	2.74	3.80	4.54	5.45		
3-EP	3.95	6.69	12.3	12.7	14.9	13.6		
2,3-DMP	3.58	6.32	7.40	9.86	8.75	8.72		
$2,4\text{-}\mathrm{DMP}$	-	-	_	1.64	—	-		
2,2-DMP	-	0.50	0.74	1.07	1.46	1.63		
3,3-DMP	1.23	1.59	2.67	2.06	2.18	2.42		

b) H₂ carrier gas

$\underset{C_{7}H_{16}}{\operatorname{Starting}}$	Benzene/toluene at T (K)						
	633	648	663	678	693		
<i>n</i> -Hp		no ber	nzene		0.13		
2-MHx	0.46	0.47	0.17	0.16	0.07		
3-MHx	_	no ber	nzene				

Literature value: benzene/toluene = 1.41 (He carrier gas, *n*-heptane feed, T = 683 K) [34]

Another aromatizing reaction involving skeletal rearrangement is the formation of benzene in parallel with toluene. This degradation can be quite significant as judged from Table I. Table VII shows benzene/toluene ratios as a function of the temperature. This shows that the structure of the reactant is the most important factor determining this ratio. The outstanding benzene formation from 3-ethylpentane and 2,3-dimethylpentane shows that the necessity of skeletal rearrangement favours degradation although the correlation is not without exceptions. This supports the participation of carbenes in the reaction and so does the low benzene formation from gem-dimethylpentanes whose skeletal rearrangement should be easier via the MCKERVEY—ROONEY—SAMMAN mechanism [21].

If benzene were a secondary product formed *via* hydrogenative elimination of the side methyl group of toluene, increasing contact time and hydrogen pressures would lead to enhancement of benzene formation. Instead, benzene could be observed almost exclusively in pulse system (exception:

n-heptane, Fig. 1) and in helium only. Thus, the formation of benzene should involve a dehydrogenative route where benzene and residual surface carbon atom are formed:



The latter product deactivates the catalyst. This is shown by Fig. 12, indicating that the amount of benzene increases, and that of the methane fragment decreases with catalyst deactivation (and decreasing total conversion). A similar mechanism was suggested by LIETZ and VÖLTER [27] for low temperature demethylation. Our findings are in agreement with the fact that the desorption energy barrier of benzene formation from heptane is much higher than that of toluene production [28].

The selectivity is shifted towards C_5 -cyclization and isomerization in hydrogen. The optimum hydrogen pressure for these products is higher than the value of ~ 15 kPa for aromatics and varies as a function of the structure of the reactant (Table VIII). The close agreement for the optimum pressure for isomer and C_5 -cyclic formation is striking. The reason why 2-methylhexane is an exception is not clear.

 C_5 -cyclization is also favoured if ring closure occurs between two primary carbon atoms (Figs 1-8). This would be in agreement with the "dicarbyne" mechanism of GAULT and co-workers [10, 22, 23]. The higher optimum hydro-



Fig. 12. Conversion of n-heptane and selectivity of aromatization and methane formation during catalyst deactivation (pulse system, T = 633 K, He carrier gas, hydrocarbon pulses without subsequent regeneration)

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Initial C ₇ H ₁₆	C_5 -cyclization	C_5 -cyclic isomerization
n-Hp	22-27	22 - 27
2-MHx	32 - 37	18 - 25
3-MHx	28 - 35	30 - 40
3-EP	32 - 37	33 - 38
2,4-DMP	38 - 45	40 - 50
2,2-DMP	16 - 22	15 - 22
3,3-DMP	20 - 25	20 - 25

Optimum hydrogen pressure (kPa) for C_5 -cyclic and isomerization reactions (circulating system, T = 603 K)

gen pressure for this reaction (as compared with aromatization) contradicts this hypothesis, since dicarbynes are very strongly dissociated species. We prefer to attribute the higher reactivity of methyl groups to their less hindered rotation permitting easier ring closure and a more facile approach of the chain ends.

Our experiments (Table VIII) seem to confirm that C_5 -cyclization and C_5 -cyclic isomerization require a common "C" surface species which may not be a "ready" cyclopentane species [29]. The optimum hydrogen pressure observed should be dictated by the requirements of this surface species.

A dual site mechanism was proposed in Refs [4, 11, 12] for C_5 -cyclization, involving a single dissociation (preferably near to a tertiary carbon atom) at a "holding site". With such an adsorption, the molecule would be held "flatly" on the surface and a second active site would be responsible for cyclization. A side reaction of this half-hydrogenated species would produce olefins [11]; accordingly, their double bond would be mainly near to the tertiary C atom or, at least, in internal position. This is confirmed by Table III showing the predominance of such olefins in hydrogen (where C_5 -cyclization dominates over aromatization).

Another piece of evidence for such a surface intermediate is the predominance of the *cis*-dimethylcyclopentane isomers in the products of cyclization. This is illustrated by Table IX showing that the *trans-/cis*-ratio is shifted in favour of the *cis*-isomer for each temperature investigated. Also the different reactivities of various alkylpentanes (Figs 4—8) indicate that the rest of the molecule also plays an important role in determining its reactivity which would not be the case with "edgewise" adsorbed dicarbenes or dicarbynes. The nonreactivity of 3-methylhexane (="2-ethylpentane") is especially worth mentioning (*cf*. Figs 3 and 4). All these problems are to be tackled in detail elsewhere [33].

~	5	1
0	.5	1
\sim	0	

Initial C7H16	2,3-DMP	2,4-DMP	
Product	t/c-1,2-DMCP	t/c-1,3-DMCP	
<i>T</i> (K)			
633		1.15	
648	1.33	1.13	
663	1.39	1.09	
678	1.73	1.19	
693	2.75	1.09	

Table IX

Trans/cis ratios of dimethylcyclopentanes formed from heptane isomers (pulse system, H₂ carrier gas)

Thermodynamical equilibrium values [32]

600	4.50	1.57
700	3.69	1.47

The formation of isomers via bond shift has lower maximum yields and it shows less sharp maxima as a function of the hydrogen pressure (Figs 1 and 2; reactions nHp \rightarrow 2MHx and reverse). According to the concept of FREN-NET et al. [5], such a behaviour is characteristic of surface intermediates where the number of surface atoms participating in the reactive complex is small. This would point to an intermediate attached to a single Pt atom as suggested e.g. for the MCKERVEY—ROONEY—SAMMANN mechanism [21]. Singly dissociated species in such isomerization have been suggested by the experiments of KARPINSKI and GUCZI, too [30]. On the other hand, the sharp maxima of C₅-cyclic reactions as a function of the hydrogen pressure shows multiatomic surface sites, in agreement with the suggestions of VAN SCHAIK et al. [31]. The flat lying intermediate suggested earlier [4, 11, 12] fulfils these requirements, too.

Summarizing, the reactivity of hydrocarbons is determined mainly by its primary adsorption. This, in turn, is influenced by essentially two factors: by the structure of the reactant (length of the carbon chain, the character of its branching, the strength of various C-H and C-C bonds) and also by the state of the catalyst surface, first of all the amount and character of the hydrogen present on (or below) the surface as a nonstoichiometric component. This latter factor may play eventually a more important role as far as the character of primary adsorption is concerned. Our results are in general agreement with the assumption that the degree of dissociation of the surface intermediates is determined mainly by the amount and availability of surface hy-

drogen: more hydrogen will bring about less dissociated surface species. These species react according to their character, each reaction type involving its own type of surface intermediate. We could confirm our previous suggestion about the character of the sequence of "hydrogen sensitivity" of various reactions and assign various surface species to each reaction. In consequence of the more numerous reaction possibilities with heptane isomers (as compared with hexanes) a modification has been suggested as far as the two types of bond shift reaction are concerned.

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MECHANISM OF AMMOXIDATION OF PROPYLENE TO ACRYLONITRILE*

(SHORT COMMUNICATION)

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In the ammoxidation of propylene to acrylonitrile, nitric oxide (NO, formed from the oxidation of NH_3) can be postulated as a common intermediate. The reaction of NO with allyl radical can yield allyl oxime. Each of the two stereoisomers of the allyl oxime can undergo two major reactions: transelimination and Beckmann rearrangement. In the case of the thermodynamically more favoured trans-allyl oxime, both of these reactions lead to one and the same product, acrylonitrile. The very same reactions of the cis-allyl oxime yield hydrogen cyanide and acetonitrile, the main by-products of the commercial ammoxidation process, as also acetaldehyde and formaldehyde, which readily undergo almost complete oxidation under the process conditions. These reactions can be summarized as follows:



Details of these reaction schemes have been published elsewhere [1]. Recent experimental results from entirely different sources support the above reaction mechanism involving NO and allyl oxime as intermediates. Some of

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the practical difficulties encountered in acrylonitrile plants can also be given a rational explanation on the basis of this mechanism.

Multicomponent molybdate catalysts can undergo radical surface reconstruction during ammoxidation, as shown from XPS analysis of fresh and used catalysts [2, 3].

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REVERSAL SPILLOVER OF HYDROGEN FROM H_xM₀O₃ BRONZE: EFFECT OF THE OUTGASSING CONDITIONS*

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Hydrogen-molybdenum oxide bronzes, prepared by hydrogen spillover on Pt particles deposited onto MoO_3 , were outgassed in different conditions.

The removal of oxygen atoms from the oxide lattice as water molecules results in the formation of ill-crystallized suboxides in the external shell of the bronze particles. As a consequence, the reversible character of the bronze is affected, and the amount of hydrogen atoms occluded in the bronze lattice, that can be retroceded when brought in the presence of an acceptor molecule such as ethylene, is reduced.

Introduction

Hydrogen bronzes refer to those metal oxides which can accommodate hydrogen atoms in their lattice. Several oxides are susceptible to form such insertion compounds [1]. The most broadly known are those prepared from WO_3 and MoO_3 .

These compounds have been obtained by different methods. GLEMSER and LUTZ [2, 3] formed the hydrogen-tungsten oxide bronze by generating nascent hydrogen from Zn and HCl in an aqueous solution containing WO₃. An electrochemical process was used by CHEVRIER [4] and HOBBS [5].

 H_xMoO_3 and H_xWO_3 were also produced using hydrogen spillover [6-11] onto Pt particles deposited by impregnation on the oxide surface. Dissociation of hydrogen occurs on the Pt particles and the H atoms invade the oxide lattice. Using this procedure insertion coefficients x = 1.6 and 0.35 have been achieved in H_xMoO_3 and H_xWO_3 , respectively.

The hydrogen bronzes can be considered as hydrogen resorvoirs; BOND et al. [12—14] were the first who took advantage of this particularity to carry out the hydrogenation of olefins. The hydrogen atoms are supplied from this reservoir, according to a reversal spillover phenomenon, the Pt particles acting as gates through which the H atoms leave the bronze lattice.

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More recently, MARCQ et al. [15], studying the hydrogenation of ethylene, supplied additional information concerning the role of Pt, the degree of reversibility of the bronze with respect to the conditioning, and the effect of temperature and ethylene pressure on the reaction rate.

The physical and chemical properties have been investigated by several authors [16-28]. A great deal of this literature is concerned with the mobility of the hydrogen atoms in the bronze lattice, from NMR measurements.

This paper aims to focus on the effect of the conditioning of Pt/H_xMoO_3 under vacuum on the retrocession of lattice hydrogen atoms.

Experimental

Preparation of the bronze

 MoO_3 (analytical grade) was impregnated with a 0.2 *M* hexachloroplatinic acid solution in order to deposit 2 wt % Pt onto MoO_3 .

Water was slowly evaporated at 60 °C under continuous stirring. The powder was then oven-dried at 120 °C during 14 h.

The impregnated oxide was heated under vacuum at 200 °C for 2 hours in order to decompose H_2PtCl_6 . This operation was achieved in an all-glass apparatus described elsewhere [15].

The temperature was then lowered to $60 \,^{\circ}$ C and hydrogen of approximately 200 Torr was introduced into the reactor. Traces of water that could be produced during this step were removed using liquid nitrogen getter.

From the pressure drop of H_2 , the insertion coefficient was calculated. After removing the excess of hydrogen, the bronze was submitted to conditioning. Thereafter, the bronze was back-titrated with hydrogen, and C_2H_4 (from Matheson) was admitted in the reaction apparatus (total volume: 1.3 liter). The formation of C_2H_6 was followed as a function of time.

Conditioning

Three ways of conditioning the bronzes were investigated:

i) Dynamic outgassing: after bronze formation the excess of H_2 was first evacuated from the vessel. Thereafter the bronze was outgassed for increasing times and at different temperatures under a dynamic residual pressure lower than 10^{-9} Bar.

ii) Static outgassing: the bronze was first outgassed under dynamic vacuum; in the meantime, the temperature was increased from 60 $^{\circ}$ C to the desired one. When this temperature was reached, the reactor was isolated from the pumping system and the bronze was maintained at that temperature generally for 14 h. The gas phase composition was analyzed by gas chromatography.

iii) Static outgassing in the presence of a liquid nitrogen getter: the same procedure as in ii) was used, but the static outgassing was performed in the presence of a liquid N_2 getter in order to remove from the gas phase water leaving the bronze surface. At the end of this conditioning period, the quantity of water collected in the getter was analyzed by gas chromatography.

Reaction with ethylene

The reaction was carried out by circulating C_2H_4 (around 40 Torr) onto the catalyst for periods of time up to 24 h, using an all-glass recirculation apparatus.

Product analysis

The separation of H_2O , C_2H_4 and C_2H_6 was made on a porapak R column, 2.5 long and 1/8'' in diameter. The carrier gas was He. The oven temperature was programmed between 50 and 120 °C, at a rate of 8 °C/min. The catharometer temperature was 200 °C.

Symbols

The various symbols used in this paper are the following:

$n H_2$	number of millimoles of H2 occluded in the bronze
X_{in}	number of H atom per Mo atom (insertion coefficient)
$\Delta n H_{o}(tit.)$	number of millimoles of H ₂ reintroduced after outgassing the bronze
	(back-titration)
$\Delta X(\text{tit.})$	variation of X corresponding to $\Delta n H_2(tit.)$
$\Delta n \dot{\mathrm{H}}_{2}(\dot{\mathrm{H}}_{2}\mathrm{O})$	number of millimoles of H ₂ removed as H ₂ O during the conditioning
$\Delta X(\tilde{\mathrm{H}}_{2}\mathrm{O})$	variation of X corresponding to $\angle n H_2(H_2O)$

Results

Preliminary experiments detailed elsewhere [15] have shown that outgassing (dynamic) H_xMoO_3 at increasing temperatures, namely 60, 120 and 160 °C for 14 h, each thermal treatment being followed by a back-titration with hydrogen, resulted in changes of Δx (tit.) (*i.e.* the variation of X corresponding to the quantity of H_2 reinserted in the bronze during the backtitration), that were appreciable especially at 120 and 160 °C.

It was then suspected that water molecules were produced during these treatments, the oxygen atoms being necessarily supplied from the oxide lattice. Consequently, lower-oxides should be formed, which in turn should affect the catalytic performances when reacting C_2H_4 onto the bronze.

A straightforward evidence for the formation of lower oxides, for instance by X-ray diffraction, was difficult to achieve, because these bronzes are unstable in air and not well-crystallized. Therefore it was felt that the quantitative determination of water formed during the conditioning treatment, would yield information on the structural degradation that occur during outgassing, which in turn, should show up in the catalytic results.

For that purpose, three bronzes (0.8 g) prepared at $60 \,^{\circ}\text{C}$ were treated in the following ways:

i) one bronze was outgassed under dynamic vacuum at 160 °C for 14 h;

ii) the second one was outgassed at 60 °C, and thereafter the reactor was isolated from the pumping system and the temperature was raised and maintained at 160 °C for 14 h;

iii) the third bronze was treated as in ii), but the water formed during the conditioning was continuously removed from the gas phase, using a liquid nitrogen getter.

After 14 h of conditioning, the amount of water formed in ii) and iii) was determined by gas chromatography, and the three bronzes were back-titrated with N_2 . The results are given in Table I.

Obviously, more water is found using the third conditioning method, *i.e.* when the water is continuously removed from the gas phase. It should also be pointed out that the discrepancy between $\Delta n H_2(H_2O)$ and $\Delta n H_2$ (tit.) is

Table I

	Conditioning			
	Dynamic vacuum (i)	Static vacuum (ii)	Static vacuum with liquid N ₂ getter (iii)	
$X_{\rm in}$	1.44	1.63	1.55	
		0.23	0.74	
$ imes X(\mathrm{H_2O})$	_	0.07	0.26	
$ extsime n H_2$ (tit.)	0.35	0.20	0.25	
$ extsf{ } \Delta X extsf{ (tit.) }$	0.13	0.07	0.08	

Influence of the conditioning method on the amount of water formed after 14 h at 160 °C from 2% Pt/H_xMoO₃ (0.8 g)

rather appreciable in run iii), although the values of $\Delta n H_2$ (tit.) in runs ii) and iii) do not differ much.

In another set of experiments, the influence of the time and temperature of the conditioning (methods ii and iii) on the amount of water produced was investigated.

A bronze with $X_{in} = 1.55$, prepared at 60 °C, was heated at 160 °C under static vacuum (without cold trap) and the water formed was determined as a



Fig. 1. Evolution of $\Delta X(H_2O)$ as a function of the outgassing time (h) at 160 °C; open symbols: outgassing under static vacuum in the presence of a liquid N₂ getter; full symbols: outgassing under static vacuum

function of time. Three other bronzes were treated under similar conditions for different times, but in the presence of a liquid nitrogen getter.

Figure 1 shows the evolution of $\Delta X(\mathrm{H}_2\mathrm{O})$ as a function of time. The shape of the curve corresponding to the conditioning conducted without a liquid nitrogen getter (*i.e.* of a concentration gradient in the gas phase) seems to indicate that the water formed would remain adsorbed on the surface of the bronze. It could act as a barrier for the desorption towards the gas phase.

On the contrary, in the presence of a cold trap, the amount of water formed after 14 h is nearly four times as much.

The bronzes outgassed in the presence of a liquid nitrogen trap were back-titrated with hydrogen. The values given in Table II show that, after one hour of outgassing, the amount of H_2 reinserted in the bronze corresponds approximately to the amount of H_2 removed as water $[\varDelta nH_2(\text{tit.}) \simeq \varDelta nH_2$ $(H_2O)]$. This suggests that a thin surface layer of suboxides does not prevent the formation of a bronze. However, the stoichiometry in the outer shell may be different from that of the bulk.

Outgassing time (h)	1	5	14
Sample weight (g)	0.811	0.8293	0.8485
X_{in}	1.60	1.67	1.63
$\Delta n H_2(H_2O)$ (mmole)	0.08	0.27	0.74
$\Delta X(\mathrm{H_2O})$	0.03	0.10	0.26
$\Delta n \mathrm{H}_2$ (tit.) (mmole)	0.11	0.18	0.25
ΔX (tit.)	0.04	0.07	0.09

Table II

Influence of the outgassing time on the amount of water formed at 160 °C under static vacuum with liquid N_2 getter

Table III

Influence of the outgassing temperature on the amount of water formed under static vacuum with liquid N_2 getter

Outgassing temperature (°C)	120	140	150	160	180
Sample weight (g)	0.9026	0.844	0.8304	0.8485	0.8647
X_{in}	1.63	1.50	1.61	1.63	1.55
$\Delta n \mathrm{H}_2(\mathrm{H}_2\mathrm{O})$ (mmole)	0.14	0.25	0.45	0.74	0.87
$ interlaw{X(H_2O)}$	0.05	0.09	0.16	0.26	0.30
	0.18	0.34	0.36	0.25	0.28
ΔX (tit.)	0.06	0.12	0.13	0.09	0.10

For increasing conditioning times, there is an increasing discrepancy between these two values. After 14 h, only one third of the total H_2 lost as H_2O could be reinserted into the oxide lattice. This result may be accounted for by irreversible structural damage occurring in the surface layer of the bronze.

Another set of experiments has been carried out in order to study the influence of the outgassing temperature. Bronzes were prepared using the usual procedure and conditioned at different temperatures for 14 h. Thereafter they were back-titrated with hydrogen. The experimental data are given in Table III. The amount of water released increases linearly with the condition-



Fig. 2. Relationship between $\Delta X(\text{tit.})$ and $\Delta X(\text{H}_2\text{O})$



Fig. 3. X-ray patterns recorded after the formation of the bronze (A), after outgassing (static with liquid N_2 getter) at 160 °C for 14 h (B), and after back-titration with hydrogen (C)

ing temperature. The Arrhenius plot gives an activation energy of $60 \cdot 6$ Joule/mole.

The relationship between $\Delta X(\text{tit.})$ and $\Delta X(\text{H}_2\text{O})$ after 14 h of treatment is shown in Fig. 2. For $\Delta X(\text{H}_2\text{O})$ values lower than 0.1, the initial stoichiometry of the bronze is apparently restored. Beyond this value, the elimination of H_2 as water becomes irreversible. This again indicates that the bronze can no longer be restored in its initial state, probably as a result of structural lattice damage.

In order to confirm this point, X-ray diffractograms were recorded on samples taken at different steps during the conditioning in sealed tubes at room temperature. The spectra shown in Fig. 3 correspond to the initial bronze (A), the compound outgassed at 160 °C for 14 h (B) and back-titrated with H_2 (C), respectively. The outgassed bronze differs from the initial one by the presence of several diffraction lines at 2.9, 5.9, 6.25, 7.8 and 8.55 ° Θ ; the intensity of the main peaks is also weaker. The additional peaks have almost completely disappeared in the X-ray diffractogram of the back-titrated sample, but the intensity of the main peaks is not restored as in the initial bronze.

It may be concluded that outgassing the bronze brings about two important modifications: i) production of a transient phase, which is almost completely removed after back-titration, and ii) the initial bronze structure is restored partially upon back-titration. The fact that the background between $\Theta = 3^{\circ}$ and $\Theta = 6^{\circ}$ has significantly increased suggests that the material has become partially amorphous. These structural data confirm the experimental observations discussed earlier. The additional weak peaks observed in spectrum B have not been identified on the basis of the X-ray data available in the literature, but undoubtedly they are characteristic of a mixture of suboxides. The diffraction peaks of the initial bronze coincide relatively well with those given by BIRTILL and DICKENS [21] for $H_{1.68}MoO_3$.

Hydrogenation of ethylene

It can be anticipated that the structural modifications provoked by the pretreatment conditions should affect the catalytic properties.

Four bronzes ($X_{\rm in} \simeq 1.42 \pm 0.04$) prepared at 60 °C and outgassed at 120, 140, 160 and 180 °C for 14 h (dynamic outgassing) were reacted with C_2H_4 . The experimental curves, corresponding to the catalysts which were or were not back-titrated are shown in Fig. 4. As expected, back-titration and outgassing temperature affect the initial rate and the yield of C_2H_6 .

The bronzes which were submitted to various conditionings in static vacuum at several temperatures (cf. the preceding section) were back-titrated and reacted with ethylene at 160 °C. The ethane production versus time is shown in Fig. 5. Here again, it is clear that the catalyst activity is strongly MARCQ et al.: REVERSAL SPILLOVER OF HYDROGEN



Fig. 4. Influence of the conditioning temperature (dynamic) on the formation of ethane at 160 °C. Full symbols: outgassing followed by back-titration with H₂; open symbols: outgassing without back-titration. (1): Outgassing at 120 °C; (2) at 140 °C; (3): at 160 °C; (4): at 180 °C



Fig. 5. Influence of the conditioning temperature (in static vacuum with liquid N₂ getter) on the formation of ethane at 160 °C; (a) outgassing for 14 h at 120, 140, 150 and 180 °C, respectively; (b): outgassing at 160 °C for 1.5 and 14 h, respectively

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Fig. 6. Relationship between the amount of C_2H_6 (mmole/g) produced after 24 h of reaction at 160 °C and $\Delta X(H_2O)$. Full symbols: bronzes outgassed in static vacuum with liquid N_2 getter. Open symbols: outgassed in dynamic vacuum [$\Delta X(H_2O)$ values extrapolated from Fig. 2]

influenced by the temperature and how the bronze was outgassed. Indeed, for an identical conditioning temperature, the yields of C_2H_6 obtained for the bronzes pretreated in static conditions are higher than those obtained with the bronzes outgassed in dynamic vacuum (compare the curves in Fig. 5 to those in Fig. 4, with back-titration).

These results confirm that the structural modifications due to the loss of lattice oxygens as H_2O during the outgassing step have a pronounced influence on the catalytic activity, and that, the more severe the outgassing conditions, *i.e.* the structural damage, the lower is the bronze performance.

In order to illustrate this point, the amounts of C_2H_6 produced after 24 h of reaction were plotted in Fig. 6 against $\Delta X(H_2O)$ detected after outgassing. A linear relationship is obtained.

It is most important to point out that during the hydrogenation of ethylene, the quantity of water formed is almost undetectable. Traces of water were found after 24 h of reaction only, *i.e.* when the C_2H_6 formation tends towards a plateau.

Conclusions

Two main conclusions can be drawn from this study.

1. The outgassing of hydrogen-molybdenum oxide bronzes at temperature higher than 120 °C is accompanied by the formation of water molecules, in amounts that are depending on the time, temperature and method of outgassing. Upon removal of water (*i.e.* removal of oxygen atoms from the bronze lattice), irreversible structural modifications are induced: suboxides are formed and the external surface layers become partially amorphous. Back-titration with hydrogen does not restore the bronze in its initial stoichiometry.

2. The total number of H atoms which are involved in the retrocession process toward an acceptor molecule, (e.g. ethylene) is strongly dependent upon the conditions of the bronze formation and of its outgassing.

The linear relationship between the amount of water removed during the conditioning of the bronze and the yield of C₂H₆ suggests that the motion of the H atoms from the bulk toward the Pt particles is inhibited by the perturbation resulting from the conditioning. The more severe they are, the lower is the hydrogen retrocession.

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CHARACTERIZATION OF Pt CATALYSTS BY HYDROGEN ADSORPTION

COMMENTS ON USUAL PROCEDURES OF DISPERSION MEASUREMENTS+

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Hydrogen adsorption isotherms are studied on two supported Pt catalysts in an exceptionally wide range of pressure $(5 \cdot 10^{-5} - 150 \text{ Torr})$ and temperature (77 K -550 K). Thermodesorption spectra, BOUDART titration and oxygen chemisorption are also measured.

On both catalysts, isotherms are TEMKIN like, due to large decrease of the adsorption heat with coverage. For one of the catalysts the monolayer value determined from the isotherm allows to calculate on the basis of a stoichiometric ratio: number of H adsorbed atoms/number of surface metal atoms equal to 1, a dispersion value of 132% indicating a very high dispersion as well as the existence of surface Pt atom bound to more than one H atom.

Results obtained by BOUDART titration do not correspond to any simple stoichiometric ratio and depend on time and pressure.

At the light of these results, the validity of some usual procedures for measuring the dispersion of supported catalysts by H_2 adsorption and related methods are discussed, namely procedures of outgassing, distinction between "reversible" and "irreversible" forms of adsorption, extrapolation to zero pressure.

Introduction

Hydrogen adsorption on a supported metal catalyst is a very classical measurement that has three main purposes:

i) Determination of the thermodynamic parameters characterizing the hydrogen adsorbed state.

ii) Measurement of the dispersion of the metal catalysts, i.e. the ratio of the number n_s of surface metal atoms to the total metal atom number n_t through the determination of the number $n_{\rm Hm}$ of hydrogen atoms adsorbed at full coverage. That implies the knowledge of the stoichiometric ratio $H_{\rm C} =$

 $=rac{n_{
m Hm}}{n_{
m s}}$. In fact $H_{
m C}$ most often is taken as unity.

iii) Identification of the different possible adsorbed species, as a heterogeneity -either "a priori" or induced -, may have consequences on the

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catalytic activity. Temperature programmed desorption is a classical method used for this purpose.

In the present work, two Pt catalysts of very different dispersion are studied by hydrogen adsorption isotherms and thermodesorption measurements. This study is conducted in an exceptional wide range of pressure, up to seven powers of ten- and of temperature- 77 to 600 K, much wider than in most of the preceding published studies. Such wide ranges are necessary for an as complete as possible characterization of the hydrogen adsorption [1], and particularly for the determination of the variation with coverage of the enthalpy and entropy of adsorption. As, for most transition metals, the dependence of coverage with pressure is weak, the slope $d\Theta/d \log_{10} P$ is around 0.1 or less in the commonly studied temperature range [1]. Such a complete study seems particularly useful for one of the studied catalysts that is the first reference European catalyst Euro Pt-1.

In the literature, most studies devoted to hydrogen adsorption in a much more restricted range of experimental conditions, have the sole purpose of determining the catalyst dispersion. Our more complete study allows namely us to comment on the usual procedure of dispersion measurement based on gas — and specially hydrogen — adsorption.

Experimental

Catalysts

Two Pt catalysts are used.

The first one is the Reference Euro Pt-1. It is prepared by impregnation of SiO₂ (Sorbsil AQ U30 silica gel from CROSSFIELD Chemicals) with $(Pt(NH_3)_4Cl_2)$ in alkaline solution. Total surface area is 185 (± 10) m² g⁻¹. Platinum content of the particles (mesh size between 0.5 and 1 mm) exclusively used in the present study is 1.772×10^{20} atom Pt per gram of catalyst.

The second catalyst, Pt 10A, supported on γ -Al₂O₃ (Degussa), was prepared in the "Institut de Recherches sur la Catalyse" (Lyon, France). Its Pt content is 3.1×10^{20} atom Pt per gram of catalyst.

Both catalysts are reduced in situ by flowing H_2 at 300 °C. Preliminary measurements showed that more drastic treatment — higher temperature of reduction, preliminary oxidation at more or less high temperature — have no influence on the hydrogen adsorption capacity of both catalysts.

Apparatus and procedures

Apparatus

The all Pyrex glass apparatus is shown schematically in Fig. 1. Main features are:

1) Glass valves with stainless steel bellows and viton seals, no greased stopcocks.

2) Evacuation through an oil diffusion pump. Back diffusion of the oil to the catalyst is prevented by a cold cap above the pump and a cold trap at 190 K.

3) Possibility of baking the whole apparatus up to 180° (high temperature limit for the viton seals of the valves) allowing to obtain a vacuum in the low 10^{-7} Torr range in the whole apparatus.

4) Three pressure gauges:

- a quartz Bourdon gauge (Texas Instrument with a range 0-260 Torr, and a limit of sensitivity of $\simeq 10^{-3}$ Torr;

- a differentially mounted Pirani gauge (range: 10⁻⁵-10⁻¹ Torr);

- an ionization gauge.



Fig. 1. Apparatus

5) Two different reactors containing different amounts of catalyst:

— the low pressure reactor, with a volume around 150 cm³ may be evacuated with a pumping speed at the catalyst level (not at the output of the pump) around 10 liters/sec for H₂. It contains an amount of catalyst corresponding to a few square meters of metal. Practical pressure range of measurement is $5 \times 10^{-5} < P < 5$ Torr;

— the high pressure reactor, with much smaller volume ($\simeq 20 \text{ cm}^3$), contains a much higher amount of catalyst ($\simeq 100 \text{ square meters of metal}$), but the pumping speed at the catalyst level is only of a few cm³ sec⁻¹.

Practical pressure range of measurement is $200 \gtrsim P \gtrsim 10^{-2}$ Torr. Range of operating pressures for both reactors overlaps in the $1 \text{ Torr} - 10^{-2}$ Torr range so that reproducibility from one sample to the other as well as of the outgassing and measuring procedures can be checked.

Isotherm procedure

Isotherms are measured mainly in the desorption mode but it is checked in a few cases with narrower pressure ranges that identical results are obtained in the adsorption mode.

In the high pressure reactor, desorption isotherms are measured using a classical volumetric procedure. In the low pressure reactor, similar volumetric procedure is used down to around 5×10^{-3} Torr; at lower pressures the catalyst is evacuated through a fixed leak (a few tens of cm³ sec⁻¹) the conductance of which is much smaller than the pumping speed of the catalyst for hydrogen (always larger than 10 liters sec⁻¹); under such conditions, a quasi equilibrium does exist between gaseous and adsorbed phases. Amount of hydrogen evacuated is measured behind the leak by the ionization gauge that has been calibrated against the Pirani gauge and the response of which is integrated.

Before any isotherm measurement, the catalyst is outgassed at 350 °C for 15 hours. The residual pressure at this temperature is in the 10^{-7} Torr range measured just above the catalyst.

Procedure for thermodesorption spectrum measurements

A quite similar procedure is used for obtaining the thermal desorption spectrum. A given amount of hydrogen is admitted to the catalyst, generally at room temperature. The catalyst is then cooled to 77 K where the H_2 amount in the gas phase is really negligible as compared to the adsorbed amount. The system is then evacuated through a fixed leak of 70 ml sec⁻¹ and the catalyst is heated at a rate in the range 10 to 40 deg C/min. Pressure is measured by a Pirani gauge and the desorbed flow measured by the ionization gauge is integrated. Temperature is measured by a thermocouple fixed at the outside of the bulb containing the catalyst. Due to the low heating rate and the low pumping speed through the leak, the thermodesorption spectrum so obtained is measured at adsorption-desorption equilibrium.

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Results

Euro Pt-1

General

First of all, three important results must be given:

i) On the pure SiO₂ support alone, at temperatures $T \ge 190$ K, adsorption is completely negligible, the adsorbed amount $n_{\rm a}$ (in molecules H₂ per gram of support) is less than 2×10^{16} at pressures P around 1 Torr. Low but significant value of $n_{\rm a}$ around 2×10^{18} molecules H₂ per gram of support is obtained at the same pressure at 77 K.

ii) Adsorption at 77 K is an activated phenomenon. When introducing H_2 on the catalyst at 77 K, n_a is 1.79×10^{20} at P = 20 Torr, but after heating to room temperature and cooling to 77 K, n_a value rises to 2.20×10^{20} at the same pressure.

iii) When H_2 is introduced at high temperature or when the catalyst is heated under H_2 pressure before isotherm measurement at a lower temperature, one observes that the adsorbed amount is systematically higher than when H_2 is introduced in the presence of the catalyst at the temperature of desorption isotherm measurement. Exact determination of the temperature T — probably around 200 °C — at which this kind of activated adsorption takes place was not undertaken but a systematic study of the effect of heating the catalyst under H_2 at 300 °C for 2 hours before isotherm measurements is described. In the next part results obtained when introducing H_2 at the isotherm temperature are reported, whereas after this part results obtained after heating at 300 °C are given.

H_2 desorption isotherms (H₂ introduction at the isotherm temperature)

Desorption isotherms are measured at the following temperatures: 77 K, 193 K, 290 K, 373 K, 450 K, 520 K and 592 K. The results are given in Figs 2 and 3 where the adsorbed amount per gram of catalyst n_a is plotted as a function of the logarithm of the pressure. All these isotherms show in a large pressure range a linear dependence between n_a and ln P, characteristic of the socalled "TEMKIN isotherm".

The isosteric heat of adsorption $Q(\Theta)$ in the range $0.45 \times 10^{20} < n_a < < 1.14 \times 10^{20}$ molecules H_2 is determined using isotherms of Fig. 2 obtained in the temperature range 193 < T < 390 K. The variation of $Q(\Theta)$ with coverage is shown on curve 1 in Fig. 4. An another determination of $Q(\Theta)$ is the following: at the end of a desorption isotherm, *i.e.* at a low pressure, the catalyst is subjected to a stepwise rise of temperature inducing a desorption; if the temperature step is small as well as the volume of the system, the induced desorption is also small; the conditions are then very close to isosteric and the



Fig. 2. H_2 adsorption isotherms on Euro Pt-1 193 K $\leq T \leq$ 592 K



Fig. 3. H₂ adsorption isotherms on Euro Pt-1 at 77 K

ratio of the pressure before and after the temperature step allows the determination of $Q(\Theta)$: the so determined $Q(\Theta)$ values are given in Fig. 1, and are in very good agreement with curve 1.

Corresponding values of the differential entropy of adsorption are also calculated and given in Fig. 5. As can be seen on Fig. 6, a compensation effect does exist between ΔS (Θ) and Q (Θ). A similar compensation effect for H₂ adsorption on Ru has already been described [21].

As the value $n_{a\infty}$ corresponding to full coverage must be close to the n_a value at high pressure on the 193 K isotherm and as the Q and ΔS values may be considered as constant in a small $\Delta \Theta$ interval near full coverage. Langmui isotherm formula is applied to the experimental points allowing to determine the $n_{a\infty}$ value: 1.17×10^{20} molecules H₂.



Fig. 4. Variation of H_2 adsorption heat on Euro Pt-1 with coverage Θ



Fig. 5. Variation of the H_2 adsorption entropy on Euro Pt-1 with coverage Acta Chim. Acad. Sci. Hung. 111, 1982



Fig. 6. Compensation effect between heat and entropy

Using this value of $n_{a\infty}$ as well as Q and ΔS values of Figs 4 and 5, the full set of isotherms can be recalculated using

$$\left(\frac{\Theta}{1-\Theta}\right)^{2} = k_{0}(\Theta) P \exp \frac{Q(\Theta)}{RT} \quad \text{with} \quad \Theta = \frac{n_{a}}{n_{a\infty}}$$
(1)
$$\ln k_{0}(\Theta) = \frac{\Delta S(\Theta)}{R} + 2 \ln \frac{\Theta}{1-\Theta}.$$

Calculated points are reported in Fig. 2, in good agreement with experimental isotherms in the temperature range 193-390 K.

It can also be seen in Fig. 2 that for the isotherms at temperatures ≥ 450 K a deviation appears between the experimental and calculated values. In fact, when considering a temperature interval larger than 193 < T < 390 K, the Clapeyron plot $\ln P = f(1/T)$ at constant coverage ceases to be linear and a lowering of the isosteric adsorption heat is observed (Fig. 7). This phenomenon must be related to the phenomenon already mentioned of a more important adsorbed amount at low temperature if hydrogen is introduced at a high temperature (see the next part). This "activated" or "high temperature" adsorption only occurs significantly at temperatures higher than 400 K. This is the reason why we did not succeed in determining the adsorption heat at low coverage ($\Theta < 0.4$). At 373 K it is possible using a very rough extrapolation, to estimate that, for example, at a low coverage Θ around 0.1, the



Fig. 7. Variation with temperature of the H₂ apparent adsorption heat on Euro Pt-1

equilibrium pressure should certainly be lower than 10^{-9} Torr, that is far from the possibilities of our apparatus. The only way to realize such low coverage values is then to measure adsorption isotherms at higher temperatures, but complication arises from the "activated" adsorption taking place.

A few remarks have also to be made coocerning the adsorption isotherms at 77 K (Fig. 3). In the low pressure domain (P < 0.1 Torr), the adsorbed amount is almost independent of the pressure. At higher pressures (P >> 1.0 Torr) a considerable increase in the adsorbed amount is observed, that must probably be related to molecular adsorption on the silica support. At high pressures the effect of temperature at which hydrogen is first introduced on the catalyst (77 K, or 290 or 573 K) is negligible. At low pressures, the effect of the temperature of introduction was already mentioned.

Desorption isotherms with introduction at high temperature ("activated" adsorption)

In these experiments, the catalyst is systematically heated for 2 hours at 573 K in the presence of a known amount of hydrogen (hydrogen pressure at 573 K around a few Torrs) before lowering the temperature to the value where desorption isotherm is measured. We did not investigate the possible effects of the temperature and the duration of the heating in hydrogen.

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In fact, for isotherms measured at temperatures higher than 450 K, we do not notice any significant difference between the so measured desorption isotherms and desorption isotherms measured by direct introduction of H_2 at the temperature of experiment. This is the reason why the results given in Fig. 8 only concern isotherms in the low temperature (T < 390 K) region where significant differences with results of Fig. 2 were observed. As seen in the figure, this difference in adsorbed quantity is approximately constant in the whole pressure domain studied and its value is close to 1.0×10^{19} molecules per gram of catalyst, in fact $\simeq 8.5\%$ in coverage.

This value is confirmed as follows:

1) the difference between calculated and measured adsorbed amount on the 450 K "normal isotherm" (see Fig. 2) is also close to 1.0×10^{19} molecules/g;

2) the dependence of the isosteric adsorption heat, determined as further on is given in Fig. 3, curve 2. In a first approximation the general shape of the $Q = f(\Theta)$ curves (1) and (2) of Fig. 3 is very similar, but curve (2) is shifted towards higher coverage by a $\Delta \Theta$ of about 1.0×10^{19} molecules/g;

3) the amount remaining adsorbed on the catalysts at 600 K and $P \simeq 20^{-5}$ Torr is also of the order of 1.0×10^{19} . But at this temperature and pressure, the adsorbed amount calculated with procedure and data of the next part should be less than 5×10^{17} molecules/g *i.e.* almost negligible. It must be noticed that, on the 600 K isotherm in the 10^{-4} —10 Torr range, the slope

 dn_a



Fig. 8. H₂ adsorption isotherms on Euro Pt-1. Influence of heating under H₂ at 570 K

of the isotherm is very small; nevertheless the catalyst can be outgassed and the surface be cleaned at the same temperature, at a pressure only two orders of magnitude lower (a few 10^{-7} Torr) within a few hours. The adsorbed amount corresponding to the "activated adsorption" is thus only very slowly desorbed and the dynamic desorption procedure in the high temperature and low pressure region does not allow to measure real equilibrium values.

Thermodesorption spectrum (TDS)

A typical TDS obtained with an initial coverage of 1.2×10^{20} molecules H_2/g ($\Theta \simeq 1.0$) is shown on Fig. 9, curve 1. Clearly, the TDS contains three wide and overlapping peaks. The low temperature one which is the less important, appears around 213 K. The largest peak appears at 365 K and a third structure appears in a shoulder around 495 K. All temperatures mentioned are measured with a thermocouple fixed to the external part of the bulb, as near as possible to the catalyst, the real temperature of the catalyst is certainly lower and the temperature difference between catalyst and thermocouple may certainly reach a few tens of degrees C.

We have studied the influence of different factors on the position and amplitude of the different peaks.



Fig. 9. Thermal desorption spectrum of H₂ on Euro Pt-1

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Influence of the initial coverage

In Table I are given the results of a series of TDS with increasing initial coverages n_a , with indication of the temperature and the pressure of the peak maximum, as well as of the amount desorbed at 623 K (when measured).

The major conclusions to be drawn from this Table are:

— The low temperature peak, always small is only observed at high coverage ($\Theta > 0.8$).

— The high and medium temperature peaks shift towards higher temperatures when the coverage diminishes.

— At 623 K and at a pressure around 10^{-5} Torr a part of hydrogen amounting to about 0.5 to 1.0×10^{19} molecules/g is not desorbed.

— Medium and high temperature peaks are poorly resolved. For low initial coverage, medium temperature peak appears as a shoulder on the high temperature one. For high initial coverage, the high temperature peak appears as a shoulder on the medium temperature one. Both have about the same importance for initial coverage around $\Theta = 0.5$.

Influence of the adsorption of hydrogen at 300 °C

In these experiments, a known amount of H_2 is introduced on the catalyst at 300 °C for one hour, then the whole system is cooled to 77 K and programmed heating is set up. In Table II the thermodesorption spectra obtained in this way are given for two different values of the coverage and may be compared with the corresponding values in Table I.

Two conclusions may be drawn from these results:

— After heating at 300 °C, an important shift of the peaks towards high temperature is observed, more than 120 K for coverage $\simeq 4 \times 10^{19}$, around 60 K for coverage around 2×10^{19} molecules/g.

— The amount of H_2 not desorbed at 350 °C (end of thermodesorption) is more important after heating at 300 °C.

Oxygen chemisorption

Adsorption of O_2 is studied at temperatures 193, 290, 326 and 430 K and at a pressure around 1.3 Torr. Results are shown in Fig. 10. Part of the adsorption is slow and the adsorbed amount increases with temperature.

BOUDART titration

BOUDART titration [12] is also performed on different samples at room temperature in the pressure range 10–20 Torr, where close to monolayer coverage in H₂ is achieved. $n_{a\infty}$ value is 11.7×10^{20} (±0.05) molecule H₂/g.

100	1 1		T
Ta	b	le	1

No.	Initial coverage	Amount	Temperature T_m (K) and pressure (Torr $\times 10^3$) for the three TDS peaks P_1 , P_2 and P_3 observed							
	at 77 K (**)	desorbed at 623 K	P	1	P_2		P_3			
		(**)	T	Р	T	P	T	P		
21	0.97	0.45					576	1.03		
7	1.35	*					541	2.11		
20^{+}	2.11	1.59			378 SS	0.86	536	4.14		
25	2.65	2.24			389 SS	1.5	509	5.03		
6	2.81	*					511	5.03		
12	3.92	*			383 SS	3.4	491	7.1		
14	4.16	3.62			405 SS	4.8	485	6.60		
5	5.14	*			396 S	6.90	472	8.10		
32^{+}	5.40	4.55			436	8.6	472	8.6		
16	6.52	6.11			395	8.7	495 S	12.3		
9	9.25	*	265	8.0	371	16.2	496 S	9.8		
2^{+}	12.0	*	213	7.3	365	15.7	495 S	9.4		

Thermodesorption spectrum. Effect of initial coverage

 $^+$ see also Fig. 9; * not measured; ** molec. $\rm H_2$ per $\rm g \times 10^{-19};$ S: shoulder; SS: small shoulder

Table II

No. Initial coverage at 77 K $\times 10^{-10}$ molec. H ₂ per gram	Initial coverage at	Amount desorbed	Te	mperature (K) and for the TI	pressure (To OS peaks	rr×10 ³)
	77 K×10 ⁻¹⁹ molec. H ₂ per gram	at 623 $K \times 10^{-19}$ molec. H ₂ per gram		P2		P_3
		<i>T</i> (K)	P (Torr)×10 ³	<i>T</i> (K)	$P(Torr) \times 10^3$	
13	3.80	* *	526	6.4	606	5.0
15	4.08	2.91	525	6.5	610	5.26
19	2.16	1.14	_	_	585	3.4
31	2.10	1.01	_	_	599	3.0

Thermodesorption spectrum. Effect of $\rm H_2$ adsorption at 330 $^\circ C^*$

 \ast Experiments 13 and 15 are to be compared with experiments 12 and 14 of Table I, experiments 19 and 31 with experiments 20 of Table I.

** Not measured.

Following ratios of O_2 chemisorption (O_c) or H_2 titration (H_T) to hydrogen monolayer $n_{a\infty}$ are found:

$$O_{\rm C}: n_{\rm a\infty}: H_T = 0.475 \ (\pm 0.25): 1.00: 1.725 \ (\pm 0.070)$$



Furthermore, it is shown that stationary values of $O_{\rm C}$ and H_T are only obtained after several hours, the kinetics of the process being also pressure dependent. O_2 chemisorption is also strongly temperature dependent.

Pt 10 A

H_2 desorption isotherms

Due to limitation on the available amount of catalyst the pressure range is, in this part of the study, limited to about 5 orders of magnitude $(10^{-5} - 2 \times 1 \text{ Torr})$.



Fig. 11. ${
m H}_2$ adsorption isotherms on Pt 10 A 193 $\leq T \leq$ 473 K

A phenomenon quite similar to the one reported with Euro Pt-1, *i.e.* a complementary adsorption of H_2 when the gas is introduced at temperature of $\simeq 100$ °C or higher, is also observed with Pt 10 A. Nevertheless, at pressures around 10^{-2} Torr or lower, the phenomenon is slow enough so that a complete set of isotherms up to 200 °C with negligible contribution of this "activated adsorption" is obtained but in a restricted pressure range. Adsorbed amounts are reported in Fig. 11 as a function of the logarithm of the pressure for temperatures 193, 290, 373 and 473 K.

The variation with coverage Θ of the isosteric heat of adsorption Q determined as in the preceding part as well as the corresponding entropy variation ΔS is given in Fig. 12.



Fig. 12. Variation with coverage of H2 adsorption heat and entropy on Pt 10 A



Fig. 13. Thermal desorption spectrum of H_2 on Pt 10 A

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The $n_{a\infty}$ value determined by the Langmuir plot of the high coverage points of the 193 K isotherm is equal to 1.08×10^{19} molecules H₂ per gram of catalyst. Using this value as well as Q and ΔS Figs 10 and 12, one may calculate using equation (1), the points indicated in Fig. 11, in good agreement with the experimental isotherms.

The "activated adsorption" measured by heating under H₂ pressure at 100 °C represents about 0.7×10^{18} molecules per gram *i.e.* 6.5% of $n_{a\infty}$.

Thermodesorption spectrum

Figure 13 shows 3 TDS spectra corresponding to three different coverages. These spectra are complex: 5 large and overlapping peaks may be distinguished. Following the initial coverage value, a given peak may appear as a shoulder of another peak or as the principal peak.

In Table III are given the results (temperature and pressure at peak maximum) of a series of TDS with increasing initial coverage.

In	nitial (molec	coverage at sules $H_2/g) \times$	$77 K 10^{-18}$	2.1*	3.35	5.15*	7.20	13.0* ^α
	1	Temp.	(1)	-	_		-	213 S
D		Press.	(2)	_	-	-	_	4.22
L	0	Temp.	(1)	-	-	-	_	258 D
F	4	Press.	(2)		_	_	_	F 5.60
		Temp.	(1)	-	-	392	324	323
	3	Press.	(2)			P 3.14	P 3.39	S 4.89
J .		Temp.	(1)	-	492	469	499	463
	4	Press.	(2)	_	P 2.44	P 2.92	P 3.22	Р 356
K ·		Temp.	(1)	543	559	546	554	553
	5	Press.	(2)	P 1.92	S 2.06	S 0.93	S 2.89	S 2.93

Table III

Thermodesorption spectrum. Effect of initial coverage (measured at 77 K)

(1) K; (2) Torr × 10³; * see also Fig. 13; S: shoulder; P: resolved peak

BOUDART titration

Due to the little amount of catalyst available and to the volume of the apparatus, BOUDART titration is performed at 2 Torr. Corresponding value of n_a (see Fig. 10) is 8×10^{18} molecules H_2 per gram of catalyst. For O_C and H_T values are: 5.4×10 molecules O_2 and 17.7×10 molecules H_2 and the ratio:

$$O_{\rm C}: n_{\rm a}: H_T$$
 is $0.675: 1: 2.22$

Let us outline the fact that O_C value is just half of the monolayer value $n_{a\infty}$.

Discussion

The discussion is divided into two parts. The first part is devoted to the properties of the catalysts we have studied. In the second part, in the light of our results, the usual procedures of measurement of hydrogen coverage and catalyst dispersion by chemisorption technique and related methods are discussed.

Properties of the Pt catalysts and comparison

Dispersion of the catalysts

For Euro Pt-1, the calculated ratio $n_{\rm Hm}$ /total Pt using $n_{\rm ax}$ value and known concentration of Pt (5.74%) lead to an "apparent" dispersion value (on the basis of a H/Pt surface atom equal to 1) of 132%. Such high apparent dispersion values have already been reported in the literature [3], [15], [16].

On the other hand, the study by electron microscopy [4] of this catalyst shows that the maximum of the particle-size distribution function as well as the volume average of the particle size lies in the range 1.6-2.0 nm that should correspond to real dispersion in the range 0.6-0.7. It has nevertheless been shown recently [22] that due to insufficient contrast, an important portion of the very small particles cannot be detected by dark-field electron microscopy. This conclusion is — a fortiori — also valid for isolated metal atoms. Thus, the dispersion as measured by electron microscopy is only a lower limit value. On the other hand it is also known that for unsupported metal catalyst made of large particles, where comparison between $n_{\rm Hm}$ and BET surface area is possible, the stoichiometric ratio $H_{\rm C}$ is close to 1 [23].

These considerations lead to the following conclusions:

i) the true dispersion of Euro Pt-1 is high, >65% at least, but probably close to 100%;

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ii) an important part of the Pt atoms at full coverage are bound to two H atoms at least. That is not impossible for atoms lying on crystal edges or even in (111) planes if every triangular set of Pt atoms defines a potential site for chemisorption of a H atom [5];

iii) the value of the real stoichiometric ratio $H_{\rm C}$ for highly dispersed catalyst remains an open question.

For Pt 10 A, apparent dispersion calculated using $n_{a\infty}$ (1.08×10¹⁹ H₂/g) and Pt concentration (3.10×10²⁰ ato s/g) is 6.75% *i.e.* a low value. Here no discussion about the stoichiometric ratio $H_{\rm C}$ is possible as no other physical information on this catalyst is available to us.

"Activated adsorption"

Both catalysts show the same phenomenon of a complementary adsorption when heating under H_2 at a temperature higher than $\simeq 400$ K for Pt 10 A, $\simeq 450$ K for Euro Pt-1. This complementary adsorption represents around 6.5% of the monolayer for Pt 10 A, $\sim 8\%$ for Euro Pt-1. In the case of Euro Pt-1, it is shown in this study that part of H_2 adsorbed under these conditions does not desorb in TDS experiments at 350 °C but prolonged heating under vacuum at the same temperature allows to obtain reproducible results and thus to desorb the high temperature adsorbed form.

Two possible explanations of this phenomenon can be given:

- adsorption of H₂ in the bulk of metal;
- spillover of H_2 on the support.

The first one seems difficult to reconcile with the high dispersion of Euro Pt-1 but cannot be rejected for Pt 10 A. For Euro Pt-1, the spillover explanation is strongly supported by a recent work [6].

Adsorption heat

It is interesting to compare the adsorption heat on two catalysts of such different dispersion. Adsorption heat at initial coverage is not measured but, by extrapolation, one may deduce similar values, around 25 kcal at $\Theta = 0$ for both catalysts. On the contrary, the variation with coverage is quite different: for Pt 10 A one observes a monotonous decrease whereas for Euro Pt-1 Q seems to remain approximately constant up to $\Theta \simeq 0.4$, then decreases steeply. A tentative explanation is that a high value of Q corresponds to low coordination Pt surface atoms that are much more numerous on a highly dispersed catalyst.

This explanation is also in agreement with the TDS results. One may assume that on Euro Pt-1, the high temperature peak corresponds to these low coordination Pt atoms, the medium temperature peak to H_2 adsorbed on

crystal faces, whereas the low temperature peak — very small in fact — should be attributed to a loosely bound form, probably molecularly adsorbed and observed only at high coverage and low temperature.

The existence of five peaks in thermodesorption on Pt 10 A is less easy to explain. Nevertheless, on the (100) planes of Pt, up to five peaks have been observed in thermodesorption at high coverage [7] whereas only one peak appeared on the (111) planes. It is thus not surprising that complex TDS are observed on a low dispersion catalyst where one would expect a lower heterogeneity, as well developed crystal faces must certainly exist on such catalyst.

Adsorption entropy

Using the adsorption entropy values of Figs 5 and 11, it is easy to calculate the entropy S_a of the adsorbed phase and to compare this value with calculated entropy [8] in adsorbed phase corresponding to different models:

- configurational entropy (immobile adsorption);

- translational entropy (mobile adsorption) calculated following either the ideal two dimensional gas model or the VOLMER model of non ideal two dimensional gas.

In these calculations, contributions to total entropy of rotational and vibrational terms are not taken into account: rotational term is really negligible for hydrogen, and considering the published values of vibration frequency of H adsorbed on metals as a correct order of magnitude, vibrational term must be always less than 1 entropy unit [9].

Results of this comparison is shown in Fig. 13. For Pt 10 A, the two dimensional ideal gas model may be rejected but, taking into account possible errors on S_a of several entropy units, it seems difficult to decide between the VOLMER model and the configurational entropy as important differences between the both models only appear at high coverage where no experimental points are available. Let us note nevertheless, in favour of the VOLMER model, that H_2 adsorption at temperatures higher than $\simeq 250$ K is considered as a mobile one [23]. For Euro Pt-1, the situation seems rather similar for coverage Θ up to around 0.75. At higher coverage experimental values of S_a increase, so that around full coverage agreement with ideal gas model seems to be good variation of S_a with coverage showing the same general shape — decreases up to $\Theta \simeq 0.75$ then increases for $0.75 \leq \Theta \leq 1.0$ — have already been described for Pt foil [24] as well as for Ni film [25], and interpreted in [24] by an increase of the vibrational entropy due to lowering of the vibration frequency.

Concluding remarks

1) The adsorbed amount of H_2 on both Pt catalysts varies linearly with the logarithm of pressure, following thus the TEMKIN isotherm. This is confirmed by the large variations of adsorption heat with coverage. Langmuir equation, most often used for evaluating hydrogen coverage in kinetic equations, may not be applied here.

2) "Activated" adsorption takes place when heating both catalysts under hydrogen at temperature around 450 K or higher, and must probably be attributed to hydrogen spillover on the support.

Comments on usual procedures of measurement of the dispersion of supported catalysts by H_2 adsorption and BOUDART titration

As the Euro Pt-1 catalyst has been studied in many European laboratories, it is now possible to compare the results and methods of the measurement of dispersion based on hydrogen adsorption. Four main topics will be discussed:

a) outgassing procedures and cleaning of the surface;

b) distinction between the so-called "reversible" and "irreversible" forms of adsorption;

c) the procedure of "extrapolation to zero pressure";

d) the BOUDART titration.

Outgassing procedure

From the H_2 adsorption isotherms of Fig. 2, one may deduce that residual pressures lower than 10^{-6} Torr at temperature around 300 °C are necessary in order to obtain a metal surface practically void of hydrogen. That is certainly not a generally accepted procedure, since the amount of adsorbed H_2 measured in our laboratory has been always significantly higher than those measured in other European laboratories.

In most laboratories adsorption measurements are performed in two types of apparatus:

i) Volumetric apparatus of the classical BET type where residual pressure at the catalyst level may be estimated in the 10^{-3} Torr range although much lower pressure are often cited in the literature. The difference is due to the fact that residual pressure is usually measured just above the pump that is connected to the bulb containing the catalyst by low conductance capillary tubings;

ii) Chromatographic apparatus (by pulse injection or frontal analysis) where H_2 pressure during outgassing is fixed by the impurity content – gen-

erally not mentioned — of the carrier gas. As 1 ppm impurity does correspond to $\simeq 10^{-3}$ Torr in partial pressure that is below detection limit of most chromatographic detectors, the residual pressure could be in most cases in the 10^{-3} Torr range.

From Fig. 2 it is clear that for residual pressures in that range temperature as high as 400 °C is necessary to obtain negligible ($\Theta < 0.01$) residual coverage. In fact it is possible to calculate an isostere corresponding to negligible coverage ($\Theta = 0.01$ for example) that relates the outgassing temperature to the residual pressure limit of the apparatus at the catalyst level. Such isostere may be calculated for every catalyst if thermodynamic data on adsorption are available. If the required temperature of outgassing of a catalyst is too high, e.g. due to sintering problems, the sole procedure is to modify the apparatus and the procedure of measurement in order to obtain lower residual pressures, by using higher conductance and pumping speed, and smaller active surface area. This problem is discussed below.

Let us mention besides that when using chromatographic techniques, O_2 impurity content of the carrier gas must also be controlled since due to the titration of adsorbed O_2 [10], [11], higher than real values for adsorbed H_2 can be obtained.

Distinction between "reversible" and "irreversible" adsorbed hydrogen

Usually, the determination of the dispersion of a catalyst [17, 18, 19] is based on the amount of so-called irreversibly adsorbed hydrogen $(H_{\rm irr})$ [14]. The common procedure of measurement is the following: total amount of adsorbed hydrogen $(H_{\rm tot})$ is first measured at room temperature, the bulb containing the catalyst is then evacuated by pumping or is flushed with an inert gas (according to the technique — volumetric or chromatographic —) at the same temperature for a short time, usually ten minutes to half an hours during evacuation reversibly adsorbed hydrogen $(H_{\rm rev})$ is assumed to desorb and can be measured in a subsequent adsorption measurement.

 $H_{\rm irr}$ is then given by $H_{\rm irr} = H_{\rm tot} - H_{\rm rev}$ In fact this procedure may be criticized from both theoretical as well as practical points of view.

From a thermodynamic point of view, every adsorption must be reversible. The term H_{rev} is then a practical one (maybe, not very well chosen) designating a part of the adsorbed hydrogen either loosely bound to the metal fixed on the support. Most people assume, without justification, that this part is not involved in the stoichiometry of the dissociative reaction of H_2 with surface metal atoms.

From a practical point of view, as shown in the following, the measurement of H_{rev} is strongly dependent upon experimental conditions. In fact,

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Table IV

Pressure	Pumping speed: (cc. \sec^{-1})									
(Torr)	1	102	104	106						
10-2	$3 \ 10^{2}$	3	$3 \ 10^{-2}$	$3 \ 10^{-4}$						
10-4	3 104	$3 \ 10^2$	3	$3 \ 10^{-2}$						
10-6	3 106	3 104	3 102	3						
10-8	3 108	3 106	3 104	$3 \ 10^2$						
10-10	3 1010	3 108	3 106	$3 \ 10^4$						

Time (in sec) necessary to realize a $\Delta \Theta = 0.01$ at different pressures and for different pumping speeds (in cc. sec⁻¹)

Given values must be multiplied by the metal surface area expressed in m²

when evacuating the catalyst after H_{tot} measurement, the H_2 pressure first decreases very rapidly, but after a few minutes reaches a very slowly decreasing but almost constant value: at this point complete elimination of H_{rev} is currently admitted. Nevertheless, this opinion was questioned in [10] where the authors wrote: "It is not clear from our data whether (a) desorption is essentially reversible . . . (b) or equilibrium prevails between H_2 gas and H adsorbed and the rate of loss of H_2 reflects the value of equilibrium H_2 ". As shown below, assumption (b) is the correct one.

The apparent irreversibility of adsorption of some part of adsorbed hydrogen results from two factors:

i) The impossibility of realizing H₂ partial pressure low enough as to correspond to negligible equilibrium coverage ($\Theta < 0.01$): a rough extrapolation of the 293 K isotherm of Figs 2 and 10 allows to estimate that the equilibrium pressure corresponding to a coverage around 0.01 is in the 10^{-12} Torr range.

ii) The duration of the evacuation necessary for desorbing most (>99%) of adsorbed hydrogen is very long. In Table IV, this duration is evaluated in the following manner: let us consider a catalyst sample where full coverage is 10^{19} molecules H_2 that corresponds to about 1 square meter of metal.* We calculate the time necessary to realize a $\Delta\Theta$ of 0.01 *i.e.* to pump 10^{17} molecules H_2 , as a function of the pressure, for different values of the pumping speed at the catalyst level. For this calculation where many orders of magnitude are involved. The pressure will be considered as constant, as, in fact,

* Corresponding for example to 1 g of catalyst containing 0.65% Pt in 100% dispersion.

for $\Delta \Theta = 0.01$, the equilibrium value of the pressure varies by less than a factor of 2.

In Table IV all values below the line of separation correspond to large or very large duration. Most studies on real catalysts are in this category, due mainly to low evacuation speed — in the range of 1 cc sec⁻¹ for chromatographic apparatus, not larger in classical volumetric apparatus with capillary tubings. That is the reason why a quasi-stationary pressure is rapidly attained when pumping on the catalyst. That is also the reason why flow rate effects such as the one described in [17], from 15 to 70 cc min⁻¹, cannot have any significant effect on $H_{\rm rev}$ measurement: orders of magnitude in the variation of flow-rate or punping speed are necessary for the $H_{\rm rev}$ value to vary noticeably.

The only possibilities for eliminating whole adsorbed hydrogen are then:

i) using simultaneously low area samples ($\simeq 1 \text{ cm}^2$) and high pumping speed (>10³ liters sec⁻¹) as in surface science studies on single crystals;

ii) or, alternatively, as in most studies on real catalysts, rising the temperature so that lower equilibrium coverages correspond to the same stationary pressure. That was indeed noted in [20] but surprisingly interpreted as the authors wrote: "an increasing part of H attached to Pt becomes reversibly adsorbed with increasing temperature".

As a conclusion, distinction between $H_{\rm rev}$ and $H_{\rm irr}$ is not justified: the total amount of adsorbed hydrogen is reversibly adsorbed. Furthermore, the value of $H_{\rm rev}$ depends on several poorly reproducible factors: amount of catalyst, duration of pumping, pumping speed at the level of the catalyst bed that is related to amount, granulometry porosity and packing of the catalyst.

Extrapolation to zero pressure

Extrapolation to zero pressure has been introduced by BENSON and BOUDART [2] when working on alumina supported Pt catalyst, in order to take into account the adsorption of H_2 by the pure alumina support, that depends linearly upon pressure. This procedure has been extended by many researchers to all measurements on supported metal catalysts, in most cases without any justification, *i.e.* without verifying that the pure support does effectively adsorb hydrogen.

For Euro Pt-1 where it has been verified that the pure SiO₂ support does not adsorb H₂ at all, it is very easy to show that the extrapolation to zero pressure may lead to conflicting results. In Fig. 14 we have plotted, in the usual way described in the literature, part of the H₂ adsorption isotherm at 290 K in Fig. 2. As linear plots do not allow to cover the high pressure range realized in our measurements, curve 1 of Fig. 14 represents the experimental points for 0.03 < P < 0.2 Torr, curve 2 these points for 0.03 < P < 2 Torr, several points in the range 0.03 < P < 0.2 are represented on both curves.



Fig. 14. Entropy of H adsorbed on Pt 10 A and Euro Pt-1. Comparison with theoretical models



Fig. 15. Extrapolation to zero pressure of a linear isotherm in two different but overlapping pressure ranges

The choice of these pressure ranges is arbitrary, similar curves are obtained at other pressure ranges either higher or lower. The general shape of both curves is very similar but the extrapolation to zero pressure is different. Similar curves have been obtained on different metal catalysts either supported or not, as well as on metal films [13].

As a conclusion, and except for the case where adsorption on the pure support may justify it, the procedure of extrapolation to zero pressure leads to results depending upon the technique used — particularly the range of studied pressure — and upon the thermodynamics of the adsorption process.

This procedure may nevertheless allow not too bad comparison between the dispersions of different catalysts of the same metal on the same support. But for that purpose, simpler method exists.

BOUDART's titration

All preceding remarks concerning outgassing procedures, distinction between reversible and irreversible adsorbed hydrogen and extrapolation to zero pressure must fully apply to the BOUDART titration. But the present work raised some new problems as several experimental facts usually not mentioned in the literature are here put in evidence:

1) O_2 "chemisorption" is time and temperature dependent. Then it is not quite certain that this reaction usually measured at room temperature is limited to the surface.

2) H_2 titration is time and pressure dependent, probably because displacement of H_2O formed on the metal and its subsequent adsorption on the support may not be complete and should possible depend upon the nature of the support. The above facts may provide at least partly an explanation to the conflicting results concerning stoichiometries of BOUDART's titration reported in the literature [20].

Concluding remarks

Measurement of the dispersion of a supported catalyst by H_2 adsorption remains a difficult problem. It involves

i) the knowledge of the stoichiometric ratio $H_{\rm C} = n_{\rm Hm}/{\rm number}$ of Pt surface atoms;

ii) the determination of the H₂ monolayer value.

Concerning the first point, if a general agreement exists on a $H_{\rm C}$ value equal to 1 for low dispersion catalysts [12], exact stoichiometry of highly dispersed catalysts is still an open question but it makes no doubt that $H_{\rm C}$ value may be significantly higher than 1.

Concerning the H_2 monolayer, best value is obtained, as done in the present work, through analysis of a full set of isotherms in a large pressure range, but that is a lengthy task. For a rapid determination, it seems that, for Pt catalyst, whatever is the dispersion, close to monolayer value of the H_2 adsorbed amount is obtained by a single measurement either at room temperature at P > 100 Torr, or at dry ice temperature around 1 Torr.

Procedures of extrapolation to zero pressure, and distinction between reversible and irreversible form of adsorbed H are complicated and lead to questionable results.

BOUDART titration is also a questionable method as its exact stoichiometry is still a matter of controversy and the results seem to depend on several experimental factors such as pressure and duration of chemisorption and titration.

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CHAIN LENGTHENING REACTIONS ON THE Pt/Al₂O₃ REFORMING TYPE CATALYST*

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Formation of toluene from *n*-hexane was studied on Pt/Al_2O_3 reforming type catalysts. Toluene selectivity data were obtained in continuous-flow and pulse reactors. The toluene formation was influenced by the thermal treatment processes applied before the catalytic reaction. High temperature hydrogen treatment strongly reduced the yields of toluene. Correlation was obtained between the ageing process induced by carbonaceous surface overlayer and the toluene formation. The reactivity of the formed carbonaceous deposits on the Pt/Al_2O_3 catalysts was studied by pyrolysis gas chromatography. Formation of toluene is discussed in terms of a surface depolymerization reaction and a new reaction mechanism is proposed.

Recently growing interest has been paid to study the chain lengthening homologation reactions [1-4], however, formation of hydrocarbons with increased chain length had been observed in earlier studies.

Formation of toluene in the reaction of *n*-hexane on Pt and Pd ribbon was observed by GRYAZNOV et al. [5-6] at relatively low temperatures in the absence of hydrogen. Studying *n*-hexane dehydrocyclization on Ni/Al₂O₃ catalysts in the absence of hydrogen traces of toluene were obtained [7-8]. The toluene formation from *n*-hexane was studied on nickel catalysts by GUCZI and co-workers [10, 11]. In recent works it has been shown that homologation of hydrocarbons takes place on different metal catalysts [4, 9], however, neither Pt films [2], Pt black [3] nor Pt/SiO₂ [4] catalysts appeared to be active in this reaction. Contrary to this recent results the formation of toluene has been observed from *n*-hexane on 0.5% Pt/Al₂O₃ catalyst modified by NaNO₂ in the absence of hydrogen using a pulse reactor [12].

With respect to the reaction mechanism the disproportionation of alkane was suggested by SACHTLER [13]. However, results obtained by GUCZI *et al.* using ¹⁴C-tracer technique [10, 11] did not support the disproportionation mechanism, and the direct alkylation of benzene was proposed. Recently it has been suggested that the reaction proceeds *via* carbenes formed by fragmen-

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tation of the initial hydrocarbon and the chain lengthening reaction can be considered as a carbene insertion into the double bond of a terminal olefin [1-3]. The hydrocarbon formed in this way with higher carbon number can further react as its precursor and *via* dehydrocyclization toluene can be formed.

In our previous works formation of toluene from *n*-hexane was observed on Pt/Al_2O_3 catalyst under the conditions of selective aromatization. It was suggested that on Pt/Al_2O_3 catalyst the carbene-alkene insertion mechanism [1-3] had less importance and other surface reactions might be involved in the toluene formation [14]. In our further study on supported platinum catalysts [15] it was demonstrated that formation of toluene from *n*-hexane could be discussed in terms of surface depolymerization of the cyclic polymeric carbonaceous overlayer formed on the catalyst, thus, formation of toluene on Pt/Al_2O_3 or other reforming type catalysts might be connected to the catalyst deactivation rather than to the olefin-carbene interaction suggested earlier.

The lack of sufficient experimental data on the role of supported platinum catalysts in the toluene formation from n-hexane prompted us to present our experimental data obtained in the course of the study of n-hexane dehydrocyclization reaction.

Experimental

Dehydrocyclization of *n*-hexane has been studied in slug-impulse and continuous-flow reactors. The reactor set-up has been described elsewhere [15-17]. Reaction products were separated on a 3.6 m long column filled with 10% DC 410 on Chromosorb P-HMDS at 325 K.

Separated on a 3.6 m long column filled with 10% DC 410 on Chromosorb P-HMDS at 325 K. Three different Pt/Al₂O₃ catalysts with 0.5% Pt content were used. Pt/Al₂O₃ (I) was prepared from PtCl₄ solution by impregnation in 0.5 M hydrochloric acid.* Pt/Al₂O₃ (II) and Pt/Al₂O₃ (III) were prepared from [(CH₃)₃PtCl]₄ by impregnation of the dehydroxylated alumina in n-hexane solution. The dehydroxylation of the methyl-platinum complex was carried out by Thermal Programmed Reaction (TPR) up to 300 °C either in nitrogen or in hydrogen atmosphere [catalyst (II) and (III), respectively]. The heating rate was 15 °C/min.

Before the catalytic reaction the catalysts were treated using the following standard procedure. First the catalysts were calcined in oxygen flow at a definite temperature for one hour. The temperature was then raised or lowered in nitrogen flow to the temperature of hydrogen treatment and nitrogen was replaced by hydrogen.

The catalyst samples were treated in hydrogen for 1.5 hours. In each run fresh catalyst samples has been used. Numbers in parenthesis indicate the temperature of oxygen and hydrogen treatment, respectively.

The amount of hydrogen chemisorbed was determined by thermal programmed desorption method. Catalysts were analysed for their chlorine content after pretreatment processes.

The reactivity of the carbon deposits formed on the catalyst in the continuous-flow experiments was studied by pyrolysis gas chromatography. Further details of this method are described elsewhere [18]. Applying this method it was established that catalysts Pt/Al_2O_3 (II) and (III) after their preparation contain trace amount of carbon deposits. The carbon content of catalyst (II) was higher than that of catalyst (III), although their absolute amount was not determined.

The characteristic data of our catalysts are summarized in Table I.

* After impregnation the $\rm Pt/Al_2O_3$ (I) catalyst was dried at 125 °C and was reduced in hydrogen at 400 °C.

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	Preparatio	Temperature treatme	Chlorine					
Catalyst	6		Initial	Final		content final	Carbon content	H/Pt*
	Irom	in	1	02	H_2			
Pt/Al ₂ O ₃ (I)	H_2PtCl_6	HCl	H ₂ (400)	400	500	1.06	_	1.78
				400	575	0.86	—	1.43
				500	500	0.96	_	1.91
Pt/Al_2O_3 (II)	[(CH ₃) ₃ PtCl] ₄	<i>n</i> -C ₆ H ₁₄	${f N_2}$ (up to 300 by					
			TPR)	400	500	-	trace**	2.50
Pt/Al_2O_3 (III)	$[(CH_3)_3PtCl]_4$	<i>n</i> -C ₆ H ₁₄	${ m H_2}$ (up to $300~{ m by}$					
			TPR)	400	500	-	trace**	2.50

Table I

Characterization of the Pt/Al₂O₃ catalysts

* Measured by thermal programmed desorption after cooling in hydrogen atmosphere.

** Carbon content of catalyst (II) is about five times higher than that of catalyst (III).

Results

Conversion and selectivity data of *n*-hexane dehydrocyclization measured on Pt/Al_2O_3 (I) catalyst in the continuous flow reactors are summarized in Table II. Formation of toluene was observed in all experiments, however, its yield has been influenced by the reaction conditions and the catalyst treatment procedure.

Formation of toluene on Pt/Al₂O₃ catalyst has been increased by

- (i) increasing feed rate
- (ii) decreasing the temperature of oxygen treatment
- (iii) decreasing the temperature of hydrogen treatment and
- (iv) increasing the reaction temperature.

One of the most striking experimental data is a sharp decrease in the methane and toluene formation as the reaction proceeds, although, in some experiments formation of toluene passes through a definite maximum. The pronounced formation of toluene at the beginning of the reaction intended us to study this reaction by the slug-pulse method, which can give more reliable information on the activity of the "fresh" catalysts. This method can also give a possibility to compare the activity of the "fresh" and "used" catalyst thus the ageing phenomena can also be modelled. Conversion data and yields measured in the first impulses on Pt/Al_2O_3 (I) catalyst are summarized in Table III.

No.	Pretre tempe	eatment erature °C]	Reaction temperature	Feed rate	Time [min]	Conver-		Select	ivities [%	1	
	02	H_2		[n .]		[%]	$\Sigma(C_1-C_5)$	i-C ₆	МСР	В	т
					1	98.9	21.0	_		78.3	0.7
1.	400	500	500	3.2	30	82.5	21.8	15.8	4.0	48.5	9.9
					60	71.1	21.2	21.0	8.4	43.7	5.6
					1	98.5	21.2	_	_	78.4	
2.	400	575	500	3.2	30	78.1	19.5	12.4	5.5	59.2	3.4
					60	72.3	16.3	17.2	8.3	54.9	3.3
					3	100.0	39.0	_	_	56.0	5.0
3.	400	500	500	1.5	46	94.6	48.5	4.8	0.9	43.8	2.0
					90	85.2	48.4	8.0	3.5	38.1	2.0
					3	100.0	62.0	_	_	35.6	2.4
4.	400	500	425	1.5	46	97.3	58.8	9.9	1.0	29.1	1.2
					90	96.7	56.4	13.7	1.0	27.9	0.9
					3	100.0	37.1	_		59.5	3.4
5.	500	500	500	1.5	46	95.0	49.6	1.4	-	46.6	2.4
					90	85.0	50.0	6.0	1.7	40.6	1.7

 Table II

 n-Hexane dehydrocyclization on Pt/Al_2O_3 (I) catalyst in continuous flow reactor

Amount of catalyst: 0.5 g; H: CH = 5:1; i-C₆ = 2-methylpentane + 3-methylpentane + 2,3-dimethylbutane; B = benzene; MCP = methylcyclopentane; T = toluene

 Table III

 n-Hexane dehydrocyclization on Pt/Al_2O_3 (I) catalyst in slug-pulse reactor

No.	Temperature of					Sal	Solastivities [0/]				
	pretreat	tment reaction		Conver-		561	lectivities [%	1			
		[°C]					MCD	D	T		
	0 ₂	H_2			$2(C_1 - C_5)$ <i>i</i> - C_6	MCF	Б	ľ			
1.	400	500	370	50.0	10.0	40.0	15.0	32.0	2.8		
2.	400	500	440	74.0	8.7	20.0	4.3	56.0	9.3		
3.	400	500	480	92.0	12.0	3.3	0.7	69.0	11.0		
4.	400	600	480	79.0	4.9	8.1	2.2	78.0	5.8		
5.	300	500	480	77.0	11.0	5.7	1.7	68.0	13.0		
6.	600	500	480	97.0	17.0	1.6	0.5	75.0	6.1		

Amount of catalyst: 0.22 g; $H_2: CH = 5: 1$; results obtained in the first pulses under quasi-stationary conditions



Fig. 1. Trends in toluene selectivities obtained in slug-pulse experiments: (1) — oxygen treatment at 400 °C, hydrogen treatment at 500 °C; (2) — hydrogen treatment at 500 °C, reaction at 480 °C; (3) — oxygen treatment at 400 °C, reaction at 480 °C. Results obtained in the first pulses; $H_2 : CH = 5 : 1$

As it can be seen that the yield of toluene, the chain-lengthening product, can be compared with the yields of other by-products as cracking products, methyl-cyclopentane and *iso*-hexanes. Below 370 °C the formation of toluene on Pt/Al_2O_3 catalyst was negligible. It could also be established that homologation took place under the conditions of selective aromatization, thus, conditions of "deep" fragmentation, as proposed earlier [1-3], was not a necessity for the chain-lengthening reaction.

More systematic data on the toluene formation on the Pt/Al_2O_3 (I) catalyst are presented in Fig. 1, where selectivities for toluene formation are shown as a function of the conversion and the influence of the reaction temperature and temperatures of oxygen and hydrogen treatments on the toluene selectivity can be demonstrated.

The trends observed in the pulse reactor were the same as obtained in the continuous flow experiments.

The influence of ageing on toluene formation has also been studied by the slug-pulse method comparing the activity of the catalysts as well as the yields of toluene formation on the "fresh" and "used" catalysts. The ageing involved loss of catalytic activity and change in the selectivity data as well as the influence of the temperature of hydrogen treatment on the ageing can be characterized comparing the $K^{\circ}/K^{\circ\circ}$ and $Y_{i}^{\circ}/Y_{i}^{\circ\circ}$ data *i.e.* ratios of the

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activity (or yield) of the "fresh" catalyst to the activity (or yield) of the "used" catalyst. Results measured on the Pt/Al_2O_3 (I) catalyst treated in oxygen at 400 °C are shown in Table IV. The yield of toluene possesses the highest

Table IV

Catalyst ageing on Pt/Al₂O₃ (I) catalyst in slug-pulse reactor Ageing induced activity and selectivity changes

No. catalyst	Temperature of hydrogen treatment	$X^{\circ}/X^{\circ \circ}$	$(S^{\circ}/S^{\circ \circ})_{\mathbf{B}}$	$(S^{\circ}/S^{\circ\circ})\Sigma$	$(S^{\circ}/S^{\circ\circ})_{\mathbb{I}}$	$(S^{\circ}/S^{\circ\circ})_{\mathbf{T}}$
1.	400	1.19	0.91	1.28	0.55	2.00
2.	480	1.20	1.01	1.00	0.45	1.80
3.	500	1.21	1.11	1.02	0.45	1.64
4.	600	1.75	1.27	0.72	0.50	1.13

Temperature of oxygen treatment: 400 °C

Reaction temperature: 480 °C

X- conversion; o - data measured in the first pulse; oo - data measured in the 15 -20th pulses

B - benzene; Σ - cracking products; I - iso-hexanes; T - toluene



Fig. 2. Conversion curves obtained at different reaction temperatures: (1) – oxygen treatment at 500 °C, hydrogen treatment at 500 °C; (2) – oxygen treatment at 400 °C, hydrogen treatment at 500 °C; (3) – oxygen treatment at 400 °C, hydrogen treatment at 575 °C. Feed rate: 1.5 hour⁻¹. Amount of catalyst: 0.5 g



Fig. 3. Selectivity changes as function of the reaction temperature: a) catalyst treated in oxygen and hydrogen at 400 and 500 $^{\circ}$ C, respectively; b) catalyst treated in oxygen and hydrogen at 400 and 575 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 and 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 and 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen and hydrogen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen at 500 $^{\circ}$ C, respectively; c) catalyst treated in oxygen at 500 $^{\circ}$ C.

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 $Y_j^{\circ}/Y_j^{\circ\circ}$ value. The ageing-induced activity loss expressed in $K^{\circ}/K^{\circ\circ}$ ratio appeared to be higher on the catalyst treated in hydrogen at higher temperature. The highest extent of loss in the toluene yields with ageing is in agreement with our results obtained in the continuous flow reactor, where very fast decrease in the toluene yields has been observed.

The influence of the thermal treatment processes on the catalyst ageing was also studied in a continuous flow reactor at different reaction temperatures. Results obtained on Pt/Al_2O_3 (I) catalyst after treatment processes (400, 500), (400, 575), (500, 500) are shown in Fig. 2. Under our experimental conditions between 425 and 500 °C the ageing process appeared to be more pronounced in the following order:

Selectivity data obtained after 45 minutes and 240 minutes on stream are shown in Fig. 3. In these series of experiments the yield of toluene increased upon increasing the reaction temperatures. After 60 minutes of reaction no significant changes were observed in toluene formation. The differences in toluene yields were more pronounced in the first 30-40 minutes, which is shown in Fig. 4 for the series of experiments carried out at 425, 450 and 500 °C on Pt/Al_2O_3 (I) catalysts after different thermal treatment procedures.

Comparing selectivity changes at different reaction temperatures it can be seen that the thermal treatment processes not only control the ageing process



Fig. 4. Toluene yields as a function of the reaction temperature and temperature of hydrogen treatment. Oxygen treatment at 400 °C. a) hydrogen treatment at 500 °C, b) hydrogen treatment at 575 °C. Reaction temperatures: (1) - 500 °C; (2) - 450 °C; (3) - 425 °C. Catalyst: Pt/Al₂O₃ (I)

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Fig. 5. Change in selectivities after carburation with ethane and ethylene catalyst treated in oxygen and hydrogen at 400 and 500 °C, respectively. A – carburation with ethane, B – carburation with ethylene. I – reaction temperature: 500 °C, II – reaction temperature: 450 °C

but change the reaction selectivities in different way depending on the reaction temperature. Thus, the formed carbonaceous overlayer possesses a definite influence on the overall catalytic performance.

To study the influence of the carbonaceous deposits on the catalytic activity and selectivity data as well as on the toluene formation the Pt/Al_2O_3 (I) catalysts treated at (500, 500) were tested after carburation by ethylene and ethane in the presence of hydrogen at the temperature of reaction for one hour.

The *n*-hexane dehydrocyclization reaction was carried out at 450 and 500 °C. Results obtained in these series of experiments are shown in Fig. 5. Our data demonstrate that the reaction paths involved ageing and the carburation induced ageing resulted in the same trends in the change of selectivity

values. Formation of toluene has been significantly reduced on the carburated catalysts as it is shown in Fig. 6.

The observed differences on the ethane and ethylene pretreated catalyst may indicate the differences between the forms of carbonaceous overlayers formed during the carburation procedure. The differences in the reactionproduct distribution, as well as in the surface reaction in the course of the carburation process may be responsible for the observed differences in the selectivity data. During carburation with ethane, methane was the only reaction product, while ethylene resulted in minor amount of higher hydrocarbons, including benzene, however, their formation ceased entirely as the carburation proceeded.

On our Pt/Al_2O_3 (I) catalyst the formation of unsaturated alkenes was negligible, however, our $[(CH_3)_3PtCl]_4$ originated catalysts Pt/Al_2O_3 (II) and Pt/Al_2O_3 (III) showed high dehydrogenation activity, *i.e.* the yield of hexenes was comparable with the yields of methylcyclopentane and *iso*-hexanes. The differences in product selectivities between these catalysts are shown in Fig. 7. Based on the carbene olefin insertion mechanism one would expect higher yield of toluene on these catalysts, however, on these catalysts the formation of



Fig. 6. Influence of carburation on the toluene yield: I — reaction temperature: 500 °C, II — reaction temperature: 450 °C, $(1) - Pt/Al_2O_3(I)$, (2) - after carburation with ethylene, (3) - after carburation with ethane



Fig. 7. Comparison of selectivity data obtained on different Pt/Al_2O_3 catalysts. Reaction time: 240 min; reaction temperature: 500 °C; catalyst treated in hydrogen at 500 °C (oxygen treatment is omitted). Conversion data on I, II and III: 41.2, 44.3, 32.6; toluene selectivities: 1.72, 1.47 and 1.70, respectively



Fig. 8. Pulse reactor data in the prestationary, quasi-stationary and post-stationary periods. (Data shown as a function of time on stream.) (1) — Total reactor outlet (response function); (2) — benzene; (3) — toluene (10x); (4) — methane (50x). Selectivities on catalyst No. 2 relative toluene yields: (5) — catalyst No.1; (6) — No. 2. Relative rates of ageing (K^0/K^{00}) No. 1 - 1.26; No. 2 — 1.48

toluene even at the beginning of the reaction appeared to be less than that of on the Pt/Al_2O_3 (I) catalyst.

The lack of increased amount of toluene on catalysts with higher dehydrogenation activity, can be considered as an indirect evidence against the carbene-olefin interactions. Although our experimental data have already given

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sufficient indirect evidences for the correlation between the catalyst ageing and toluene formation we have further experimental data to support our suggestion that the formation of toluene can be related to the catalyst ageing.

In our slug-pulse method the pulse was a square-like function for the reaction inlet (I) as shown in Fig. 8. The reactor outlet (R) had a response function, which consisted of three definite parts: pre-stationary (I), quasistationary (II) and post-stationary (III) periods. Results obtained in the quasi-stationary (II) periods were discussed before, however, further information was furnished by product distributions measured in the (I) and (III) periods shown in Fig. 8. In period (I) the formation of benzene and cracking products precedes the formation of toluene and the stationarity in toluene formation needs longer time to be achieved. From the sequence of the appearance of the reaction products the strength of adsorption of the products surface intermediates can be evaluated, consequently in the formation of toluene a strongly retained surface species should be involved.

In period (III) the amount of toluene in the reactor outlet decreases only slightly, while the total reactor output as well as the amount of benzene and methane show a sharp decrease. On catalyst sample N° 2 the formation of higher alkyl-aromatic hydrocarbons ($C_8 - C_{10}$) was also observed in trace amounts. Additional information was obtained by comparing the relative yield of toluene measured in two experiments shown also in Fig. 8. The relative yields were calculated as the ratio of the formed toluene to the reactor outlet. On our catalyst samples the relative yield of toluene was high and increased in the same order (N° 1 < N° 2) as the rate of catalyst deactivation expressed in $K^{\circ}/K^{\circ\circ}$ ratios.

Discussion

Our experimental data clearly demonstrated the formation of toluene, the chain lengthening product, on platinum containing alumina supported catalysts under condition of selective aromatization.

With respect to the mechanism of toluene formation benzene alkylation with monocarbon fragments on the surface has been proposed [9]. Recently it has been suggested that carbene like species and terminal olefins are involved in the toluene formation and a carbene insertion mechanism via metallocyclobutane intermediate has been proposed [1-4]. Under our experimental conditions we did not observe an increase in toluene yield on catalysts producing unsaturated hydrocarbons in higher amounts. As well as no heptane formation was found. We could not obtain any experimental evidence supporting the carbene-olefin insertion mechanism. We observed a certain build-up period in our continuous flow experiments when the total amount of products leaving the reactor is less than the amount of hexane introduced. The formation of

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toluene was more pronounced in this period. The build-up period can be related to the formation of an unknown surface overlayer, which can consist of different surface species from C1 to C6 as well as carbonaceous polymeric entities with different extent of dehydrogenation and strength of adsorption. Thus, we suggest the formation of those species which may be responsible for the toluene formation in this build-up period. Furthermore, the increased relative yield of toluene in the post-stationary period measured in slug-pulse experiments (Fig. 8) may be considered as further evidence, that in the formation of toluene a strongly bonded polymeric carbonaceous surface overlayer, responsible for ageing, should be involved. Formation of higher alkyl aromatic hydrocarbons and substituted naphthalene derivatives in trace amount gave further support on the cyclic structure of this overlayer. Consequently, we consider that toluene and other alkyl aromatic as well as condensed aromatic hydrocarbons can be considered as products of hydrodepolymerization of the cyclic polymeric carbonaceous surface overlayer. In the build-up period mentioned above although selectivity towards benzene formation is high, relatively large amount of methane has been formed. Formation of relatively large amount of methane can be explained assuming the formation of a multiply bonded, partly dehydrogenated C6 entity on the fresh platinum catalyst covered with hydrogen. This multiply bonded species in the presence of available surface hydrogen can react with C-C bond rupture with the formation of methane.

In order to understand the role of the carbonaceous surface overlayer as well as the role of ageing processes in toluene formation the influence of the high temperature hydrogen treatment on the ageing processes should be discussed. In the literature no data is available with respect to the role of the strongly chemisorbed hydrogen, formed at high temperature, in the catalyst ageing. We have observed higher deactivation rates on catalysts treated in hydrogen atmosphere at higher temperatures. We also observed decrease in catalytic activity and in hydrogenolysis selectivity upon increasing temperature of hydrogen treatment. Decrease in methane formation was even more pronounced. Our TPD experiments also demonstrated an increase in the amount of strongly chemisorbed hydrogen, however, the total amount of the adsorbed hydrogen detected by TPR was less after high temperature hydrogen treatment. Explanation given by MENON and FROMENT [19, 20] can be applied to discuss our experimental results.

The loss of total activity on Pt/Al_2O_3 catalysts upon increasing the temperature of hydrogen treatment can be attributed partly to the self-poisoning by the strongly chemisorbed hydrogen. It can also be established that following high temperature hydrogen treatment the mobility of the overall hydrogen pool is diminished. The lowered mobility may be responsible for the suppression of the main hydrogen consuming reactions, *i.e.* the formation of methane and

hydrodepolymerization of the formed carbonaceous polymeric overlayer. Upon suppressing of both reactions the rate of ageing may increase. In the absence of available hydrogen the C_1 surface species can take part in the surface polymerization reaction. Probably, this type of surface reactions takes place under carburation with ethane or ethylene.

The mobility of the surface hydrogen can be decreased by the carbonaceous overlayer itself. Probably this change in the mobility may be responsible at least partly for the increased ageing process and decrease in toluene formation on carburized catalysts.

In the absence of mobile hydrogen and presence of the stronger form of chemisorbed hydrogen the primarily formed carbonaceous polymeric overlayer can be further dehydrogenated with the formation of more strongly bonded surface hydrocarbon residue, *i.e.* the ageing process becomes more pronounced. Thus, the formation of toluene can be considered as a reaction which decreases the ageing process.

In the literature there are only scarce data on the reactivity of surface carbonaceous overlayer in oxidizing or reducing atmosphere. In order to prove our hypothesis on the role of depolymerization of surface carbonaceous overlayer in the toluene formation we applied flash pyrolysis in hydrogen atmosphere using pyrolysis gas chromatography. According to our proposed reaction routes, for the formation of toluene in hydrogen atmosphere and at

	Catalysts*					
	Pt/Al_2O_3 (I) +	Pt/Al_2O_3 (I) + Al_2O_3				
	+ quartz	$\mathbf{Pt}/\mathbf{Al}_{2}\mathbf{O}_{3}$	$\mathrm{Al}_2\mathrm{O}_3^{**}$			
$\Sigma C, \ \mu g^{***}$	40.79	65.55	14.39			
$C_1 + C_2, \%$	75.65	86.77	51.42			
C ₃ , %	6.20	3.49	13.62			
B, %	8.72	2.92	7.15			
T, %	2.74	2.22	3.68			
$\frac{C_1+C_2}{B+T}$	6.59	16.82	4.74			
$\frac{\mathrm{C_1}+\mathrm{C_2}}{\mathrm{C_3}}$	12.20	24.80	3.78			
B	3.18	1.32	1.94			

Table V

Reactivity of different surface carbon overlayers studied by pyrolysis gas chromatography

* The catalyst bed was diluted with quartz and Al₂O₃.

** Carbon overlayer formed on pure alumina.

*** Amount of total reaction products, expressed in carbon equivalent. Reaction temperature: 500 °C; catalyst pretreatment: (500, 500); reaction time: 4 hours. Pyrolysis in hydrogen at 900 °C, time of pyrolysis: 10 sec; B - benzene, T - toluene.

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	Experimental conditions					
	n-Hexane dehydro- cyclization	Ethane* treatment	Ethane treatment + + n-hexane dehydro- cyclization			
Σ C, μ g	103.56	89.21	77.65			
$C_1 + C_2, \ \%$	62.87	71.92	64.54			
C3, %	11.63	3.37	4.10			
B, %	5.92	6.91	4.79			
Т, %	4.10	3.23	2.19			
$\frac{C_1+C_2}{B+T}$	6.27	7.09	9.20			
$\frac{C_1+C_2}{C_3}$	5.41	21.34	15.74			
B T	1.44	2.14	2.19			

Influence of carburation on the reactivity of surface carbon overlayers Pyrolysis GC data

Table VI

Reaction temperature: 475 °C; pretreatment (500, 500)

* After 1 hour treatment with $H_2: C_2H_6 = 5:1$ hydrogen-ethane mixture.

higher temperatures, the surface "carbon" reacting with hydrogen should give alkyl aromatic hydrocarbons. In Table V the pyrolysis products of the surface carbonaceous overlayer are shown for different Pt/Al_2O_3 catalysts. As it can be seen toluene can be considered as one of the characteristic reaction products. The most striking data is the formation of benzene and toluene on the platinum free carrier.

It appeared very interesting to compare the reactivity of the surface carbonaceous overlayer formed

- (i) in *n*-hexane dehydrocyclization,
- (ii) after carburizing with ethane,
- (iii) in *n*-hexane dehydrocyclization after carburizing with ethane.

These results are summarized in Table VI Significant changes have been observed in the reaction products. The ratios of the reaction products also altered. It indicated that the ethane-originated carbonaceous overlayer may also have a cyclic type surface structure. This surface overlayer reacting with hydrogen can give benzene, toluene and higher alkyl aromatics.

With respect to the mechanism of toluene formation as well as of formation of higher alkyl aromatics we can not exclude the involvement of carbene-like CH_x ($x \le 2$) or C_2H_y ($y \le 4$) species, which can react with a strongly dehydrogenated cyclic C_6 surface intermediate.

Additionally, we may suggest that all of the alkyl aromatics and condensed aromatics can also be formed from one precursor, *i.e.* from a polymeric MARGITFALVI et al.: CHAIN LENGTHENING REACTIONS



Reaction Scheme Scheme 1

cyclic surface overlayer partly responsible for the catalyst deactivation and the following reaction scheme is proposed (see Reaction Scheme). Accepting the consecutive dehydrogenation route for *n*-hexane dehydrocyclization [22] from "transoid" hexadienes chemisorbed on the catalyst, formation of benzene is hindered. However, these species can be involved in methane formation (routes 4, 5) provided there is available hydrogen at the catalyst surface, or in a further dehydrogenation step (route 6) it can be converted to a polymeric cyclic surface overlayer [23]. If there is no available hydrogen on the catalyst surface further dehydrogenation of this overlayer can take place (route 7). However, in the presence of available hydrogen depolymerization of these cyclic species can take place (route 8 and 9) with the formation of toluene and other alkyl aromatics as well as methane, $C_2 - C_5$ hydrocarbons, hexane and benzene as it has been obtained in the post-stationary period in the slug-pulse experiments or in the flash pyrolysis experiments. At higher temperatures

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both routes may have an importance, while at lower temperatures route 9 has only minor importance. These cyclic carbonaceous overlayers may also be formed from lower hydrocarbons as methane, ethane and ethylene too. In this case in the formation of surface carbon the strongly dehydrogenated C₁ species may be involved and the cyclic structure can be formed by step by step addition of these species (routes 10 and 11). If this C_1 species is strongly bonded to the surface, probably, it can be considered as an electron-deficient surface species. This electron deficiency can result in the scavenger effect, *i.e.* suppressing the formation of toluene observed in the case of the carburized catalysts. The lower toluene yields on carburized catalysts can also be attributed to the decrease in the reactivity of the overall surface hydrogen pool. However, to propose more detailed mechanism of ageing-involved surface reactions more detailed studies on the Pt-C-H ternary system are needed.

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HYDROGENATION OF CO₂ ON Rh/Al₂O₃

STUDY OF THE FORMATION AND REACTIVITY OF SURFACE SPECIES OF THE REACTION*

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The synthesis of methane from H_2 and CO_2 was investigated on alumina supported Rh catalyst. Special attention was paid to the identification of surface species formed during the reaction or surface interaction. Infrared spectroscopic measurements revealed that linear and bridged CO, and adsorbed formate species were present on the surface. The formation of surface carbon was also detected during the reaction. Evidences are presented to show that the surface formate is located on the support.

Detailed measurements were performed concerning the reactivity and possible roles of these surface species in the catalytic reactions. On the basis of the results obtained the possible modes of the hydrogenation of CO_2 are discussed.

Introduction

The current energy problem has initiated renewed interest in coal as an energy source, in its conversion to $H_2 + CO$ and in the hydrocarbon synthesis via the Fischer-Tropsch reaction. Although the Fischer-Tropsch process is at present regarded as a high cost route from coal to liquid fuel, it is estimated that most of the cost is associated with synthesis gas (H_2 and CO) production [1].

In view of this problem it seemed promising to turn to CO_2 , as an alternative carbon source the production of which does not require coal and its conversion to synthesis gas. Another factor is that we have large fields of natural carbon dioxide, the catalytic transformation of which into more valuable carbon containing compounds seemed to be of great technological importance. When this work was started in our laboratory there was very little information on the hydrogenation of CO_2 in the literature.

In the first part of our work we investigated the hydrogenation of CO_2 on alumina supported noble metals [2-5]. We found that specific rates for the formation of CH_4 (expressed in terms of turnover number, rates per unit surface area of metals) decreased in the order Ru Rh Pt Ir Pd [3].

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This order is somewhat different from that found by VANNICE [6] (Ru Rh Pd Pt Ir) for the formation of CH_4 from a $CO + H_2$ gas mixture at the same temperature and under very similar conditions. In the comparison of our data with those obtained by VANNICE, the following was established: the specific activities (N_{CH_4}) of Ru, Pt and Ir agreed strikingly in the two reactions. The activation energies differed appreciably only on Ru. The catalytic behaviours of Rh and Pd, however, were markedly different in the two processes. In the case of the $H_2 + CO$ reaction their specific activities are the same, and about one order of magnitude less than that of the most active Ru. On the other hand, the specific activity of Rh for the hydrogenation of CO_2 is two orders of magnitude higher than that of Pd; and about six times higher than in the production of CH_4 from the $H_2 + CO$ mixture. The activity of Pd, which was found to be the least effective catalyst for the formation of CH_4 in the $H_2 + CO_2$ reaction, is more than one order of magnitude lower than in the $H_2 + CO$ reaction.

In order to establish the reason of the high efficiency of Rh catalyst and the possible mechanism of the hydrogenation of CO_2 , we investigated the low temperature interaction of $H_2 + CO_2$ and paid a great attention to the identification of surface species formed during the reaction.

By means of infrared spectroscopy we detected adsorbed CO and adsorbed formate ion. By chemical analysis, the presence of surface carbon was confirmed.

In this paper we give an account of the characteristics of the formation of these surface species, we compare their behaviours with those observed during the adsorption of these compounds in the absence of H_2 and then we examine their reactivity and possible roles in the catalytic reactions.

Experimental

Materials

The catalysts were prepared by impregnating alumina (Degussa P 110 Cl) support with a solution of $RhCl_3 \cdot 3H_2O$ to yield a nominal 1 and 5 wt. % metal. The impregnated powders were dried at 373 K. Before any measurements the catalysts were oxidized for 30 min and reduced for 60 min at 673 K *in situ*. For infrared studies, transparent thin wafers (30×10 mm) were prepared at high pressure.

Methods

Infrared spectra were recorded by a Specord 75 IR double-beam spectrometer (Zeiss, Jena). In a Kiselev-type infrared cell all spectra were recorded at the temperature of the infrared beam at \sim 313 K. In the high-, and low-temperature cell constructed in our laboratory, the spectra were taken at the reaction temperature in vacuum or in the gas flow.

In the study of the reaction of adsorbed formate species a specially designed microcell was used. The small volume of the cell (~ 15 mL) made it possible to flush the gas phase entirely into the gas-chromatographic column.

Adsorption measurements were carried out in a Sartorius microbalance. The hydrogenation of CO_2 and CO was studied in a flow micro-reactor at atmospheric pressure. Temperature programmed reaction (TPR) experiments were also performed in this reactor. The dispro-

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portionation of CO and the reactivity of surface carbon were investigated in a microcatalytic pulse system.

The pulse reactor was incorporated between the sample inlet and the analytical column of the gas chromatograph. The percentage exposed (the dispersity) of rhodium was determined by H_2 adsorption at 298 K by use of a dynamic impulse method [4]. The dispersity of 5% Rh/Al₂O₃ was 30.2% and that of 1% Rh/Al₂O₃ was 33.2%.

Results and Discussion

Formation of adsorbed CO

Upon admitting of the $H_2 + CO_2$ mixture (3.3 kPa of each gas) into the cell at 300-373 K, the following spectral changes occurred. Even at the beginning of the adsorption, new bands appeared between 2020-2039, and at 1870 cm⁻¹ (Fig. 1). On raising the adsorption temperature the intensity of the band between 2020 and 2039 cm⁻¹ increased up to 388 K, but it decreased above this temperature.

It is to be mentioned that these bands were not detected on pure alumina under the same conditions.

In order to facilitate the interpretation of the above results, we examined the infrared spectra of adsorbed CO recorded under the same conditions. Infrared spectroscopic measurements on the adsorption of CO over Rh/Al_2O_3 unequivocally show that at least three kinds of adsorbed CO exist on the surface [7–16]: a twin structure, Rh, absorbing at 2101 and 2035 cm⁻¹;



Fig. 1. (A) Infrared spectra observed at room temperature after adsorption of CO₂ and H₂+CO₂
(1:1) on Rh/Al₂O₃. (A) (1) base, (2) 3.3 kPa CO₂ at 298 K, (3) 6.65 kPa H₂+CO₂ at 298 K, (4) at 373 K, (B) 5.3 kPa CO₂+H₂ (1:1) at different temperatures for 5 min



Fig. 2. Infrared spectra observed at room temperature after adsorption of CO of different pressure (A) on 5% Rh/Al₂O₃ at 298 K (spectrum 2) and 373 K (spectra 3-5), (B) on 1% Rh/Al₂O₃ at 298 K

a linear form, Rh–CO, absorbing at 2060–2070 cm⁻¹; and a bridged form, Rh \searrow

CO yielding a broad band at 1855-1870 cm⁻¹. The most interesting Rh

feature of the adsorption of CO is the formation of the twin structure.

As the spectra in Fig. 2 show, the above surface species were formed on samples used in the present work, too. The doublet due to the twin structure appeared at 2104 and 2035 cm⁻¹. Their intensities were almost equal. Weak bands due to bridged CO appeared at 1860–1870 cm⁻¹, and linearly bonded CO produced a band at 2060–2070 cm⁻¹. Figure 2 also shows that the formation of these surface species depends on the Rh content, *i.e.* on the dispersion of Rh, as in the case of 1% Rh/Al₂O₃ mainly the twin band appeared in the spectrum.

On comparison of these spectra with that obtained after coadsorption of the $H_2 + CO_2$ mixture, the following can be stated about the latter spectrum:

(i) the doublet due to twin CO was completely missing;

(ii) the linearly bonded CO appeared at a somewhat lower frequency, $2020-2039 \text{ cm}^{-1}$;

(iii) no significant change could be observed in the appearance of bridged CO.

We obtained similar spectra during the catalytic reaction, at 473-573 K. The intensity of linearly bonded CO was somewhat less and appeared at 2020 cm⁻¹.

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We propose the following explanation for the above feature of the spectra [16, 17]. The absence of the twin structure can not be attributed to the low surface concentration of CO, as these surface structures appeared at all coverages of CO (Fig. 2). It is more probable that the adsorbed hydrogen prevents

the formation of the twin structure, and that instead $\operatorname{Rh}_{CO}^{H}$ or $\operatorname{Rh}_{CO}^{H}$

is formed. The fact that the vibration of this species is somewhat lower than that of unperturbed linearly bonded CO is in agreement with the expectation that the H chemisorbed to the rhodium atom of a carbonyl is electron-donating, which increases the π -donation from the rhodium into the antibonding π orbital of the CO, resulting in a decrease in $v_{\rm CO}$.

An alternative view represented by some Japanese workers [18] is that the appearance of CO bands at lower frequencies is exclusively due to the coverage effect. This argument is based on the results of SOMORJAI and DUBOIS [19] on Rh single crystals. Although there is no doubt that this is an existing effect, nevertheless on the basis of several observations we believe that the different IR spectra of adsorbed CO formed in the $H_2 + CO_2$ surface interaction and in the reaction can not be attributed merely to the low coverage of CO.

The phenomena of the absence of twin CO and the appearance of terminal CO at lower frequencies on Rh are not unique for the $H_2 + CO_2$ interaction (or for CO₂ adsorption as IIZUKA and TANAKA [18] conclude) the same behaviour was experienced in other cases, when adsorbed CO was produced in a surface reaction on Rh.

The decomposition of adsorbed formic acid on alumina-supported Rh yielding CO, CO₂, H₂ and H₂O as products, gave a CO band at 2030-2040 cm⁻¹ and a weaker one at 1875 cm⁻¹, but never a twin CO band at all. Similarly as in the case of the H₂ + CO₂ interaction, the band intensity of linear CO was significantly higher than that observed at high CO₂ exposure, but the band still appeared at lower frequency. Similar observation was made in the study of the adsorption and decomposition of H₂CO on Rh/Al₂O₃ [20].

In addition, YANG and GARLAND [21] found that the presence of hydrogen shifts the 2062 cm⁻¹ band (terminal CO) to lower frequencies, 2038–2027 cm⁻¹, at 433 K, without causing any decrease in its intensity.

It is to be mentioned, however, that the admission of even 0.6-13 Pa CO at 300 K onto a surface treated with the $H_2 + CO_2$ gas mixture at 373 K for 10 hours produced a twin band at 2104 and 2038 cm⁻¹. This may indicate that the CO formed in the $H_2 + CO_2$ surface reaction adsorbs on different sites, or in the presence of a larger amount of CO the adsorbed hydrogen will be replaced by CO.

Formation of adsorbed formate

Upon introduction of the $H_2 + CO_2$ reactant gas mixture absorption bands also appeared at 1375, 1395 and 1596 cm⁻¹. Weak bands were also observed at 2914–2910 cm⁻¹ (Fig. 1). As the adsorption of HCOOH on Rh/Al₂O₃ and on Al₂O₃ support alone produced exactly the same absorption bands, the 1596 and 1380 cm⁻¹ bands are assigned to the asymmetric and symmetric O–C–O stretching vibrations of adsorbed formate ion. The 1395 cm⁻¹ band relates to a CH deformation mode, while the weak band at 2914– 2921 cm⁻¹ is attributed to the CH stretching vibration.

In the presence of the $H_2 + CO_2$ gas mixture weak formate bands appeared even at 300 K. The intensities for formate bands grew with the increase of the adsorption (reaction) time and temperature up to 423 K. From the temperature dependence of the initial rate an apparent activation energy of 17.6 kJ/mol was calculated for the formation of formate ion (Fig. 3). Above this temperature, when the CH_4 formation was detectable, their intensities decreased. At given temperature and gas composition, however, the intensities of formate bands varied only little with the reaction time; their position was remarkably constant during the reaction.

The fact that the location and behaviour of the formate bands resulting from the $H_2 + CO_2$ interaction on supported Rh fully agrees with those observed following the adsorption of formic acid on the Al₂O₃ support alone suggests that the formate ion resides not on the Rh, but rather on the oxide support. This conclusion seems to be corroborated by the quantitative determination of the surface formate-ion concentration using AMENOMIYA's correlation [22] between



Fig. 3. Arrhenius plots of formate formation for Rh/Al₂O₃

the absorbance of the formate band (1596 cm⁻¹) and the amount of formate ion; at saturation at 373 K the number of formate groups on Rh/Al_2O_3 was found to be 5 times higher than the number of surface Rh atoms.

The question is still open, however, as to whether the formate ion is totally bonded to the support or whether part of it occupies a fraction of the Rh.

In order to answer this question we investigated the $H_2 + CO_2$ interaction and the adsorption of HCOOH on Rh/SiO₂. As shown previously by many workers, SiO₂ adsorbs HCOOH in a molecular form [23, 24] and only to a small extent, in contrast to many other oxides (Al₂O₃, MgO, ZnO, TiO₂ *etc.*). The adsorbed HCOOH is relatively weakly held to the SiO₂; adsorption of HCOOH on Rh/SiO₂ and on SiO₂ alone at 298 K produced a band at 1720 cm⁻¹ which was easily eliminated by evacuation at 298 K. We found no indication for the formate ion on Rh/SiO₂ at 298-573 K, at any pressure of HCOOH or $H_2 + CO_2$ mixture. As we have no reason to assume that the adsorption of formic acid should be basically different on Rh supported by Al₂O₃, in the light of the results obtained on Rh/SiO₂ we may safely conclude that the formate ion is unstable on Rh and that the formate bands found for alumina supported Rh sample relate exclusively to formate ion bonded to the support.

This conclusion is supported by our recent Auger and electron energy loss measurements on clean Rh foil under ultrahigh vacuum conditions [25]. Adsorption of formic acid on Rh at 110 K produced intense losses at 11.6 eV; it disappeared, however, above 270 K, indicating the high instability of formate groups on Rh.

The formation of surface carbon

Carbon formation could not be detected after adsorption of CO_2 (1.3-53 kPa) on reduced Rh/Al₂O₃ at 300-573 K. In the presence of H₂, however, there were some indications for the formation of surface carbon at the temperatures (523-573 K) of the catalytic reaction.

Its amount was determined in the following way: after the catalytic run had been completed, the $H_2 + CO_2 + He$ flow was replaced with He and the sample was kept in He flow for 10–20 min at 548 K, which according to IR spectroscopic measurements are sufficient to remove all chemisorbed species from the catalyst surface. Afterwards He was replaced with a $H_2 + He$ stream. The formation of CH_4 observed is due to the hydrogenation of surface carbon formed in the $H_2 + CO_2$ reaction.

In order to establish the effects of the reaction time and the temperature on the carbon deposit, the Rh samples were treated with the reactant gas mixture under the same conditions, and the surface was then reacted with H_2 pulses (1 mL) in a He flow until CH_4 formation ceased. Some results are shown in Fig. 4. The amount of carbon deposited increased initially but soon reached a steady value. Its limiting ratio to the number of surface Rh atoms, $C/Rh_{(s)}$,



Fig. 4. The amount of surface carbon formed in the $H_2 + CO_2$ reaction at 573 K on Rh/Al₂O₃ at different reaction times. The amount of carbon was determined in the form of CH_4 by treating the surface with H_2 . The sample was flushed with He before H_2 introduction.

was 0.26. It is to be mentioned that during the hydrogenation of CO the amount of the carbon deposit on Rh samples at 473-573 K was about 3-5 times higher than in this case.

As it seemed very likely that the formation of surface carbon in $H_2 + CO_2$ reaction occurred through the formation and dissociation of CO, we investigated this process separately on Rh/Al₂O₃ catalyst.

Disproportionation of CO

The process was investigated first by the pulse technique. One CO pulse contained 41.6 μ mol CO, which was 3.8 times larger than that of surface Rh atoms. The extent of CO disproportionation was based on the determination of CO₂ evolved.

A considerable amount of CO adsorbs at 298—473 K on reduced Rh/Al_2O_3 surface, but only very small amount of CO_2 ($\sim 1\%$ of CO) was found in the effluent at 473 K. Subsequent CO pulse did not produce CO_2 indicating that neither disproportionation nor dissociation of CO occurred at this temperature. The disproportionation of CO, however, took place at higher temperatures. At 548 K, about 10% of CO pulse disproportionated.

Attempts were made to determine the apparent activation energy of CO disproportionation on 1% Rh/Al₂O₃. This was done in a flow system at 553 — —623 K. CO (~ 10%) was added to a flowing stream of helium, and CO₂ formation was followed in time. The rate of CO₂ formation declined very quickly in the first minutes but after 3—6 minutes reached a nearly constant value (Fig. 5). The activation energy of the CO disproportionation was calculated from the steady state rate of CO₂ formation; we obtained 37 kJ/mol. Note that HARRIOT and VAN HO [27] obtained 41.8 and 50 kJ/mol for the same process on 25% Ni/SiO₂.

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Fig. 5. The CO_2 evolution as a result of CO disproportionation on 1% Rh/Al₂O₃ (10% CO in He stream); (A) at 623 K (B) at 593 K

The reactivity of surface species detected

The reactivity of the adsorbed CO

The hydrogenation of adsorbed CO on Rh/Al_2O_3 has been studied by FUJIMOTO *et al.* [26]. They have found that the "bridge" CO was hydrogenated at lower temperatures than the "linear" CO to form hydrocarbons consisting mainly of methane. The "twin" CO on Rh/Al_2O_3 desorbed without being hydrogenated. It is very likely, however, that these results reflect only the susceptibility of the adsorbed CO towards dissociation. This process can be promoted by activated hydrogen. In this respect it is important to mention that the surface carbon can be hydrogenated to CH_4 even at 300—373 K, where no hydrogenation of adsorbed CO was observed (see later).

The reactivity of the adsorbed formate

We have shown before that the surface formate ion formed in the H_2+CO_2 reaction resides not on the Rh but on the alumina support. In spite of the location of the formate group, however, it can not be considered a *totally inactive* surface species. As the surface concentration of formate group on Rh/Al₂O₃ remained the same even after 5 or 13 hours of reaction, it seems very likely that this surface concentration represent a steady-state value.

Isotope substitution experiments confirm this view. On replacing the H_2 in the reacting gas mixture with D_2 at 473—523 K, the C—H bands at

2914 and 2850 cm⁻¹ and the formate C—H deformation band at 1395 cm⁻¹ decreased in intensity. In parallel, new bands appeared at 2200-2100 cm⁻¹ (C—D stretching), indicating the occurrence of the decomposition of HCOO- and the formation of DCOO⁻ species [28].

It appears to be important that these shifts occurred only at the temperatures where the methane formation proceeded; below these temperatures the shifts occurred very slowly.

These observations are in contrast with those of DALLA BETTA and SHELEF [29] on Ru/Al_2O_3 . In this case the infrared bands due to formate ion were formed slowly and continued to grow in intensity even after the reaction had reached a steady-state. In addition, no isotope substitution was observed during the reaction.

Another important observation is that in the presence of H_2 the stability of the formate decreased appreciably, and simultaneously CH_4 was formed (Fig. 6). This was clearly manifested at 425 K, when the decomposition of surface formate is slow and the methanation of CO is negligible; hydrogen



Fig. 6. Changes in the intensity of formate band (1595 cm⁻¹) (A) at 423 K (C) at 523 K. (B) Changes in the surface concentration of formate ion and the amount of methane formed on Rh/Al_2O_3 in the presence of H_2 at 423 K

activated by Rh, however, can react with formate adsorbed on the support to yield methane [30]. In the temperature range of methanation reaction on Rh/Al_2O_3 , however, the stability of formate ion is considerably less, and only a small fraction of it reacts with activated hydrogen (Fig. 6).

As the decomposition of adsorbed formate yields CO and CO_2 in this temperature range, it can not be established with certainty whether the slight CH_4 formation is a result of hydrogenation of adsorbed formate through a different surface complex, or whether it is a product of hydrogenation of CO or CO_2 formed in the decomposition of adsorbed formate.

Taking into account all these observations and results, we may conclude that the surface formate is a by-product of the $H_2 + CO_2$ reaction; its surface concentration is controlled by the temperature and pressures of the reacting gases. It seems very likely that the production of CH_4 and other hydrocarbons in the hydrogenation of CO_2 on supported Rh occurs only to a negligible extent through the formation and reactions of surface formate. This view is further supported by the observation that the formation of the formate ion was not detected on Rh/SiO₂ at either temperatures, although the hydrogenation of CO_2 proceeded rapidly on this sample above 573 K.

The reactivity of the surface carbon

In the subsequent measurements we investigated the reactivity of surface carbon formed in the disproportionation of CO on supported Rh samples. Carbon was produced by injection of CO pulses (5-10) in He stream flowing over the reduced Rh samples at 548 K. The amounts of CO₂ formed and that of CO unreacted were determined. Afterwards the reactor was flushed with He at 548 K for 10 min, which according to IR spectroscopic studies, are sufficient to remove adsorbed gases, then cooled in He flow to different temperatures.

The reactivity of surface carbon was investigated first by pulse technique in He flow until CH_4 formation ceased, or decreased to very small values. It appears that a small part of surface carbon (1-2%) can be hydrogenated to CH_4 on Rh/Al_2O_3 at room temperature. At higher temperatures the methane formation was more pronounced. At 548 K about 80% of surface carbon reacted with the first H_2 pulse. Treating the surface with additional H_2 pulses produced CH_4 in decreasing quantities. Raising the temperature to 623—673 K, we still observed a slight CH_4 formation which indicates that some parts of carbon are very unreactive towards H_2 .

The activation energy of the hydrogenation of surface carbon on Rh/Al₂O₃ has been determined *in a flow system*. The amount of surface carbon produced was kept constant (\sim 20 μ mol/g catalyst) in every experiment. This corresponds to a coverage of about 0.60—0.9 of a monolayer. The results are shown in Fig. 7.

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Fig. 7. (A) Rates of carbon hydrogenation over 1% Rh/Al₂O₃ at different temperatures. (B) TPR spectra with H₂ following carbon deposition by exposure of 1% Rh/Al₂O₃ to 5 CO pulses at 548 K (1) and at 603 K (2)

It appears that depending on the temperature about 10-24% of surface carbon react with H₂ in a very fast process in the temperature range of 442—513 K. The amount of surface carbon reacted in this stage increases with the rise of temperature. The value of activation energy determined from the temperature dependence of the initial rate of methane formation (methane formation extrapolated to zero time) was 54 kJ/mol.

The results of these measurements showed that different kinds of surface carbon exist on the surface. In order to confirm this assumption and to determine the reactivities of different carbons the method of *temperature programmed reaction* (TPR) spectroscopy was used.

Some characteristic TPR spectra are also shown in Fig. 7. It appears that, from the point of reactivity, several forms of surface carbon can be distinguished. A very little formation of CH_4 was registered at 303—323 K (we designate this stage with α_1). The main stage of CH_4 formation was observed at 423—593 K, $T_{\text{max}} = 515$ K (α_2) with a small peak at 690 K (β). When Rh samples were exposed to CO at 603 K, the reactivity of surface carbon formed was much less. In these cases the α_2 peak became very small, and the majority of carbon reacted in the β stage.

A possible mechanism of hydrogenation of CO_{2}

On the basis of these results we propose that the following elementary steps are occurring in the methanation of CO_2 on Rh/Al_2O_3 . (* represents the active sites for adsorption and reaction)

$$H_{2(g)} + 2 \ast \rightarrow 2 H - \ast$$
 (1)

$$CO_{2(g)} + * \rightarrow CO_2 - *$$
 (2)

$$2 H - * + CO_{2(g)} \rightarrow \frac{CO}{H} * + OH - *$$
(3)

$$\mathrm{H} - \ast + \mathrm{CO}_{2(\mathrm{g})} \rightarrow \mathrm{HCOO} - \ast \tag{4a}$$

$$H - * + CO_2 - * \rightarrow HCOO - * + *$$
(4b)

$$HCOO - * + 2 H - * \rightarrow \underbrace{CO}_{H} * + H_2O + 2 *$$
(5)

$$\mathbf{C} \longrightarrow \mathbf{C} \longrightarrow [\mathbf{C}] \longrightarrow \mathbf{C}$$

$$C \longrightarrow + 2 H_{2(g)} \rightarrow CH_4 + *$$
(8)

$$[C] \longrightarrow + 2 \operatorname{H}_{2(g)} \rightarrow CH_4 + *$$
(9)

[C] less reactive surface carbon

As regards the role and importance of surface species formed during the catalytic reaction we can say the following:

(i) The adsorption and dissociation of CO_2 on Rh in the absence of H_2 is very limited. In the presence of H_2 , however, the dissociation of CO_2 is greatly enhanced and can be easily detected slightly above room temperature. As the rate of methanation of CO_2 is much higher than that of CO, the dissociation of CO_2 cannot be the rate-limiting step.

(ii) Although we have strong evidences, which show, that the formate group formed in the $H_2 + CO_2$ reaction locates on the alumina support, we can not exclude the possibility that the formation of CO in the $H_2 + CO_2$ reaction occurs through the formation and decomposition of formate ion. This reaction may occur at the metal/support interphase.

Our further experiments showed that the formate group can not be considered a totally inactive species in the methanation reaction, as it reacted with activated hydrogens even at 425 K yielding CH_4 .

Taking into account, however, that the formation of formate was not detected on Rh/SiO_2 at 300—673 K, although the hydrogenation of CO_2 proceeds rapidly on this sample above 470 K [5] we may conclude that the production of CH_4 occurs only to a negligible extent through the formation and direct hydrogenation of surface formate species.

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(iii) In our opinion the important steps in the hydrogenation of CO₂ are the dissociation of chemisorbed CO formed in the reaction and the subsequent hydrogenation of surface carbon. As we have shown, the disproportionation of CO does occur on $\mathrm{Rh}/\mathrm{Al_2O_3}$ at elevated temperatures, and a part of surface carbon can be hydrogenated into CH4 even at 373 K, where no hydrogenation of chemisorbed CO was experienced.

The fact that the formation of CH4 is faster and occurs with lower activation energy than when we use the $H_2 + CO$ mixture can be attributed to the differences in the surface concentration of CO and C. When we use a $H_2 + CO$ mixture, CO adsorbed on Rh can function as a poison toward hydrogen chemisorption, and hence results in a decreased methanation rate. In addition, the production of surface carbon (step 6) will be much larger, as a consequence, not all the surface carbon can be hydrogenated in the first instant, and there will be sufficient time for a part of the carbon to be transformed to less reactive forms (step 7). It is very likely that this ageing process corresponds to the transformation of carbidic carbon into the less reactive amorphous and/or graphitic form.

In the case of hydrogenation of CO₂, the concentration of adsorbed CO, and hence the concentration of surface carbon, is relatively low. The carbon formed can react rapidly with the large excess of H₂, and there is less possibility for the accumulation and aging of surface C.

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KINETICS AND MECHANISM OF CO/H₂ REACTION ON IRON-RUTHENIUM CATALYSTS PREPARED FROM BIMETALLIC CLUSTERS*

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Iron-ruthenium catalysts prepared from a mixture of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ (A), $H_2FeRu_3(CO)_{13}$ (B) and $Fe_2Ru(CO)_{12}$ (C) deposited on Cab-O-Sil from hexane solution have been investigated in the CO/H_2 reaction at different temperature, at 1 and 19 bar pressures. Catalyst A possesses the same activity as C in agreement with the composition, whereas catalyst B with the highest amount of Ru is the most active among them. All catalysts decomposed in helium have higher activity than those decomposed in hydrogen. The apparent activation energy on aged catalysts is always lower than on fresh ones which is due to the surface carbon being active in the hydrocarbon formation. The mechanism includes three types of carbons, *i.e.* those active in methane formation, in olefin formation and in deactivation. The olefin formation requires surface carbon and metallic sites together the latter being responsible for the activated form of CO adsorption, and in parallel to that, to deactivation process. The role of hydrogen on the surface is affected by the CO coverage during the reaction.

Introduction

Previously [1] we have shown that bimetallic catalysts prepared from a mixture of iron and ruthenium monometallic carbonyl clusters are more active in CO hydrogenation than the same metals prepared from aqueous solution of inorganic salts. Iron formed after the decomposition of $Fe_3(CO)_{12}$ deposited on Cab-O-Sil revealed very low activity for olefin formation [1]. On the contrary, ruthenium prepared in the same way as iron showed a very high activity but the selectivity was shifted towards the methane formation. Bimetallic catalysts showed intermediate activity but comparatively high selectivity for olefin formation. The formation of bimetallic phase beside iron oxide phase was proved by temperature programmed decomposition [1] and by Mössbauer spectroscopy [2]. It was then assumed that if bimetallic catalysts are formed from a mixture of two monometallic clusters, the behaviour concerning the decomposition spectra and the catalytic activity should be similar to those prepared from bimetallic clusters deposited in the same way.

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The suggested similarity has been proved by temperature programmed decomposition [3], however, we do not have data on the activity of these catalysts. In the present work the activity and selectivity of the catalysts prepared from $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ will be compared to that prepared from a mixture of two monometallic clusters and the mechanism of the CO/H_2 reaction will be discussed in terms of the different types of surface carbons assumed previously [4].

Experimental

Catalysts

Catalyst A was prepared in the following way: A mixture of 0.5 wt. % iron in form of $Fe_3(CO)_{12}$ and 0.5 wt. % Ru in form of $Ru_3(CO)_{12}$ was deposited from hexane solution. Cab-O-Sil HS 5 (Cabot Corporation, Massachusetts) was previously evacuated overnight at 570 K to 10^{-3} Pa. The solution containing the mixture of the carbonyl clusters was frozen and evacuated three times to remove all traces of air. At room temperature Cab-O-Sil was impregnated by the solution of clusters and the hexane was frozen out followed by overnight evacuation at room temperature. The supported carbonyl cluster was stored under CO atmosphere to minimize the decomposition due to the ambient atmosphere.

Catalysts *B* and *C* contained iron ruthenium metals in 1 wt.% prepared in the way described for catalyst *A* by using H_2 FeRu₃(CO)₁₃ and Fe₂Ru(CO)₁₂ bimetallic clusters, respectively. In atomic composition this latter one resembles to that of catalyst *A*.

All three catalysts were decomposed either in hydrogen by heating it up to 770 K or in helium heated to 570 K. The characteristics of the decomposition and the chemisorption of the catalysts prepared in this way have been given elsewhere [3].

Catalytic apparatus

Continuous flow type tubular reactor working in a differential regime at a conversion level below 1% has been used. Most of the reactions were carried out at atmospheric pressure but the catalytic apparatus could be pressurized up to 60 bar. At the effluent part of the system two sampling valves were connected in series; one of them was connected to FID to measure the total hydrocarbon production, the other was connected to a chromatographic column 4 m in length filled with *n*-octane on Porasil C to separate the hydrocarbon products. The separation was very good up to C_4 *i.e.* olefins and paraffins could be easily separated however, above C_4 the hydrocarbons could be analysed only by the carbon number. For analysis a Pacard 427 chromatograph was used connected to an integrator type Chinoin Digint μ 34. Calibration for the individual hydrocarbons were carried out and the total mol percentage for the hydrocarbons was calculated. From these values the selectivity for the individual hydrocarbons was calculated by

$$S_i = \frac{C_i}{\sum\limits_i C_i} \tag{1}$$

where C_i is the concentration of the i^{th} species in moles.

Results

Previously [3] we compared the catalytic activity of catalysts A, B and C to that containing only iron and prepared from $Fe_3(CO)_{12}$ deposited on Cab-O-Sil. These results clearly showed that the activity sequence for CO/H_2 reaction is B > C > pure iron. Simultaneously, the threshold temperature



Fig. 1. Temperature dependence of the reaction rate; (1) catalyst A decomposed in He, (2) catalyst B decomposed in He, (3) catalyst B decomposed in H₂, (4) catalyst C decomposed in He, (5) catalyst C decomposed in H₂

increases in the reverse direction. In Fig. 1 the temperature dependence of the reaction is presented. Under steady state condition, *i.e.* when the activity of the catalysts is already stabilized in the CO/H_2 reaction, catalyst A decomposed in helium appears to be the most active and catalyst C decomposed in hydrogen is the least active one. Catalyst A decomposed in helium has the same activity as catalyst C which corresponds to what we expected on the bases of the same composition of catalysts A and C. The energies of activation of the reactions are given in Table I.

All catalysts which have been decomposed in helium, possess considerably lower energy of activation for the reaction than that decomposed in hydrogen.

Previous investigations have shown [1, 5, 6] that metal carbonyl clusters decomposed in helium contain some amount of carbon encaptured in the metallic frame, thus the lower activation energy was assumed to be due to the presence of surface carbon which is active in the hydrocarbon formation.

Catalyst	Decomposition	Energy of activation kJ mol ⁻¹		
A	He/570 K	71		
B	He/570 K	71		
B	${ m H_2}/770~{ m K}$	109		
С	He/570 K	79		
C	$H_2/770~K$	102		

Table I Apparent energies of activation of $CO + H_2$ reaction

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Fig. 2. Change of the reaction rate by the time on stream at 525 K; (1) catalyst B decomposed in He, (2) catalyst B decomposed in H_2 , (3) catalyst C decomposed in He, (4) catalyst C decomposed in H_2

We have, therefore, studied the effect of time on stream on the activity of the different catalysts, and on the other hand, on the selectivity of the catalysts. In Figs 2 and 3 activity and selectivity of the main products, respectively, are presented. On the contrary to earlier study on Fe/Al_2O_3 catalysts [7, 8], here the activities continuously decreased as the catalysts were aged.

Decomposition and dispersion of the catalyst	Addition treatment and remarks	T/\mathbf{K}	$\begin{array}{c} Reaction \\ rate \\ 10^8 \ mol \\ s^{-1}g^{-1} \end{array}$	S_{C_1}	S_{C_2}	$S_{C_2} =$	S_{C_3}	$S_{C_3} =$	$S_{C_4}^+$
C	Initial	525	50	0.57	0.048	0.087	0.015	0.164	0.12
$Fe_2Ru(CO)_{12}$	Stabile	524	13	0.73	0.02	0.100	0.007	0.099	0.05
He/300	Stabile	554	43	0.69	0.035	0.112	0.006	0.10	0.05
D = 0.28	He/500	524	17	0.77	0.023	0.087	0.008	0.08	0.04
	$\rm H_2/500$	524	5.9	0.73	0.017	0.11	0.006	0.12	0.04
С	Initial	524	8.9	0.74	0.02	0.09	0.006	0.103	0.041
$H_2/500$	Stabile	526	3.0	0.81	0.01	0.07	0.009	0.098	0.032
D = 0.14	Stabile	553	10	0.73	0.016	0.097	0.01	0.119	0.028
A	Initial	527	31	0.72	0.026	0.085	0.011	0.115	0.036
$egin{array}{l} { m Ru}_3({ m CO})_{12} + \ + { m Fe}_3({ m CO})_{12} \end{array}$	Stabile	527	17	0.72	0.016	0.077	0.008	0.13	0.042
$\frac{\text{He}/300}{D = 0.6}$	Stabile	551	31	0.68	0.024	0.116	0.005	0.158	0.0015

Table II

The effect of temperature and working condition on the reaction rate and selectivity

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As far as selectivities of the three main products, methane, ethylene and propene are concerned in Fig. 3 different features are revealed. Generally speaking, on catalyst B containing 75 at % Ru methane selectivity is high and slightly decreases with time. On catalyst C containing only 33 at % ruthenium, the methane formation increases regardless of whether they were decomposed in helium or in hydrogen. Normally, ethylene formation increases, especially at the beginning of the reaction, but the selectivity value is low on catalyst B decomposed in hydrogen. The same is valid for propene formation on the same catalyst. On catalyst C prepared in helium propene formation initially is very high but after a constant decrease, the selectivity becomes similar to those characteristic of the other catalysts.



Fig. 3. Change of the selectivities by the time on stream at 525 K; (1) catalyst B decomposed in H_2 , (2) catalyst B decomposed in H_2 , (3) catalyst C decomposed in He, (4) catalyst C decomposed in H_2

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Fig. 4. Effect of the total pressure on the selectivities on catalyst B decomposed in He at 570 K; blank 1 bar pressure, shadowed 19 bar pressure

In Table II the selectivities of catalysts A and C both prepared in helium by decomposition up to 570 K are compared, as well as the effect of temperature on the selectivity in the low temperature range (below 570 K) is shown. It is interesting to note that at the beginning of the reaction catalysts A and Cbehave differently, however, in the steady state regime the selectivity values are similar to each other indicating that both catalysts behave in the same way under the same operating conditions. Temperature increase tends to decrease methane formation and accelerate olefin production.

However, when decomposition takes place up to 770 K in hydrogen the amount of methane formed initially and in the stable regime is higher than that formed on helium decomposed catalysts and simultaneously olefin is also smaller. Catalyst C shows higher activity, but, at the same time, higher methane formation after heating up the catalyst in helium. The regeneration in hydrogen tends to slightly increase the olefin formation.

The effect of pressure increase is revealed in the decrease of olefin formation and slight increase of the production of higher hydrocarbons (see Fig. 4).

Discussion

It has been proved [2, 3] that bimetallic iron-ruthenium catalysts can be prepared by decomposition of bimetallic carbonyl clusters, thus there is no doubt that in the present case our catalysts are —at least partly — bimetallic ones. It has also been proved that the catalysts decomposed in helium consist of smaller particles than those prepared by hydrogen treatment [3]. In the discussion it is, therefore, necessary to consider at least two factors, *i.e.* the ruthenium content, and the size of the metallic particles.

Previously the CO activation mechanism has been given on iron-ruthenium films deposited under UHV condition [9]. It was established that due to the lack of CO_2 in the gas phase the first step after the CO adsorption is the formation of the activated form of CO in which carbon and oxygen are loosely connected to each other, but not completely dissociated and at the same time both atoms are linked to two metal sites. The same mechanism is given as one of alternatives by DRY [10] and RAUTAVOUMA and VAN DER BAAN [11].

The following step is the reaction of oxygen in the activated form of CO with hydrogen to form water leaving the activated carbon on the surface to participate in different transformation on the surface. BILOEN also favoured this initiation mechanism because he described the initiation step as the transformation of CO molecule adsorbed initially on a single site, *i.e.* on top of a metal atom, into a strongly adsorbed state on a metallic multisite followed by the removal of oxygen in form of water [12]. The presence of this active carbon was proved also by *in situ* Mössbauer experiments [4] in which active surface species could be observed regardless of whether surface carbide had been formed or not. Previously kinetic evidence was found [4] that the active surface carbon may participate in further transformations, *i.e.* i) polymerization to form olefins and higher hydrocarbons, ii) formation of methane and iii) formation of stable carbide responsible for the deactivation of the catalysts. This is summarized in the following scheme:



where mobile and immobile surface carbons are denoted by $[C]_m$ and $[C]_i$, respectively.

The proportion of these surface species is largely influenced by the crystallite site of the catalyst as well as by the hydrogen coverage on the surface. Consequently, selectivity should be discussed in terms of the factors which influence these two parameters mentioned.

Due to the carbon retained on catalysts B and C decomposed in helium the metal dispersion is higher compared to that produced by decomposition

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in hydrogen [1, 3]. This results in a higher activity and higher selectivity for olefin formation, and for hydrocarbons of lower molecular weight. Due to the presence of carbon deposited during the decomposition and to the small particle size there is a depletion in hydrogen on the surface. The metallic sites needed for CO activation are available for mobile surface carbon formation leading mainly to olefins. Due to the small particle size ethylene and propylene are the main products. This is in agreement with BASSET's results [13] in which the main initial products are olefins with low carbon number on $Fe/Al_{2}O_{2}$ prepared from $Fe_{2}[CO]_{12}$, but as soon as the particle size increases olefin distribution shifts to higher carbon number.

Furthermore depletion in hydrogen occurs when the catalyst is stabilized. According to Scheme 1 parallel to an increase in olefin formation, deactivation also takes place. The decomposition in hydrogen favours the formation of larger crystallites, which in turn, gives way to the preferential formation of stable carbon deposit and thus to methane formation in a larger proportion.

When the catalyst composition is shifted to a ruthenium rich catalyst. hydrogen coverage increases. Thus, carbon formation is somewhat prevented in comparison to iron rich catalyst. This again decreases olefin formation and selectivity shifts to methane formation (see Fig. 3). The experimental fact, *i.e.* that the switch off carbon monoxide from the reactant mixture results in the cease of olefin production, does not mean the absence of reactive carbon on the surface, but the increase in hydrogen coverage accelerates hydrogenation of mono-carbon species rather than chain formation leading to olefins. This is in excellent agreement with the results obtained on iron ruthenium films [9], and with measurements on catalyst A carried out earlier [14]. The present experiments on catalyst B at high pressure seems to support the role of hydrogen coverage, *i.e.* by increasing the total pressure included hydrogen, the hydrogenation activity increases.

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CATALYTIC OXIDATION AND ADSORPTION OF PROPENE ON $V_2O_5(001)$ AND $V_6O_{13}(001)$ SINGLE CRYSTAL SURFACES*

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The catalytic oxidation of propene on $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces has been investigated using XPS and X-ray diffraction techniques. It has been established that V_2O_5 itself has exhibited no catalytic activity and in course the reaction the oxidation state of the catalyst decreased. V⁴⁺ ions were suspected to play an important role in the preliminary adsorption of propene. SIMS studies have confirmed that adsorption of propene requires the presence of V⁴⁺ ions on the surface.

Introduction

In the generally accepted reaction scheme for the catalytic oxidation of propene to acrolein on transition metal oxides, it is believed that the reaction proceeds through the formation of an allylic intermediate [1]. Therefore an aH has to be abstracted from propene. It is furthermore believed that stabilization of the allylic intermediate takes place on a transition metal ion, which has d-electrons available for bond formation [2]. Next, lattice oxygen is inserted, leading to acrolein formation. This is the MARS-VAN KREVELEN scheme [3], which leaves the catalyst in a reduced state. Therefore, it can be supposed that an active oxidation catalyst has weakly bound lattice oxygen and has the possibility of forming lower oxides by crystallographic shear mechanisms. As V₂O₅ contains weakly bound vanadyl lattice oxygen and easily forms lower oxides by a crystallographic shear mechanism, one could suppose that V2O5 should be an active oxidation catalyst. Both MARGOLIS and LALYA-ROVA [4] and COLPAERT [5] showed that to obtain an active oxidation catalyst, the presence of lower oxides on the catalyst surface was a necessary condition. On the other hand BUTT and KENNEY [6] confirmed that on vanadia catalysts, lattice oxygen was inserted into the hydrocarbon.

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The aim of this work was to obtain information concerning the adsorption stage of the reaction, by studying both the catalytic oxidation of propene on $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces and the adsorption of propene by secondary ion mass spectrometry on these surfaces.

The catalytic oxidation of propene into acrolein on $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces

$V_2O_5(001)$ surfaces [7]

To ensure stoichiometry of the $V_2O_5(001)$ surfaces a standard oxidizing treatment was applied: 24 hours at 850 K under 1 atm O_2 . After this treatment, the $V_2O_5(001)$ surfaces always showed a period of zero activity. X-ray diffraction and XPS showed that in this phase, only V_2O_5 was present on the catalyst surface. After a certain time, depending on the operating conditions such as *e.g.* partial pressure of propene and reaction temperature, acrolein formation starts. Both XPS and X-ray diffraction show that the catalyst is now in a reduced state. The presence of V^{4+} ions at the surface is established. As a function of time, acrolein formation goes through a maximum and decreases again. At this point, XPS and X-ray diffraction show that the¹ catalyst is now in an even further reduced state.

 $V_6O_{13}(001)$ surface

 $V_6O_{13}(001)$ surfaces, which already initially contain V⁴⁺ ions, never show a period of zero activity. Reaction is always immediate and the same product distribution is observed as in the acrolein formation stage of V_2O_5 . This product distribution on V_6O_{13} is not time dependent but temperature dependent. Above 720 K it changes and a similar product distribution is obtained as on the further reduced V_2O_5 .

Conclusion

It is clearly shown that V_2O_5 itself is not active. Reduced V_2O_5 and V_6O_{13} both are active oxidation catalysts and both contain V^{4+} ions. V_2O_5 does not contain V^{4+} ions. This could mean that V^{4+} ions play an important role in the adsorption of propene as adsorption is a necessary condition for the oxidation reaction to occur. SIMS was used to study the adsorption of propene on $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces in order to obtain information concerning the adsorption site.

Adsorption of propene on $V_2O_5(001)$ and $V_6O_{13}(001)$ single crystal surfaces

Fingerprint spectra of the clean surfaces

Before the adsorption of propene on $V_2O_5(001)$, reduced $V_2O_5(001)$ surfaces, or $V_6O_{13}(001)$ single crystal surfaces, SIMS fingerprint spectra of the clean surfaces had to be taken, in order to characterize the surface. Each surface, *i.e.* the freshly UHV cleaved $V_2O_5(001)$ surface, the reduced V_2O_5 surface and the $V_6O_{13}(001)$ surface, are characterized by a different $V_xO_y^+$ cluster intensity ratio. Furthermore a different $V_xO_y^+$ cluster intensity ratio is observed for $V_6O_{13}(001)$ surfaces in function of oxygen coverage. By comparing the SIMS results obtained on V_2O_5 surfaces with ADPSD (angular



Fig. 1. a: SIMS spectrum of a freshly UHV cleaved $V_2O_5(001)$ surface, b: SIMS spectrum of the reduced $V_2O_5(001)$ surface

dependent photon stimulated desorption of ions [8]) results, a model for the freshly cleaved and reduced V_2O_5 surfaces could be proposed. By comparing the results obtained on $V_6O_{13}(001)$ surfaces with LEED-LEIS results [9] on V_6O_{13} a surface model for the different $V_6O_{13}(001)$ surfaces could also be proposed. The SIMS spectra of the freshly UHV cleaved and the reduced $V_2O_5(001)$ surface are shown in Figs 1a and b.

Adsorption of propene on $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces

Only reduced $V_2O_5(001)$ and $V_6O_{13}(001)$ surfaces are found to adsorb propene. The appearance in the SIMS spectrum of a peak at m/e = 108, which can be identified as $VOC_3H_5^+$, on reduced $V_2O_5(001)$ surfaces confirms that the adsorption occurs in the allylic form. The SIMS spectra of a reduced $V_2O_5(001)$



Fig. 2. a: SIMS spectrum of a reduced $V_2O_5(001)$ surface, b: SIMS spectrum of a reduced $V_2O_5(001)$ surface after propene adsorption

surface before and after adsorption are shown in Figs 2a and b. As only reduced $V_2O_5(001)$ surfaces and $V_6O_{13}(001)$ surfaces adsorb propene the role of V^{4+} ions in the adsorption seems confirmed. Furthermore on $V_6O_{13}(001)$ surfaces an additional peak at m/e = 92 (VC₃H₅⁺) is found. The oxygen coverage of the $V_6O_{13}(001)$ surface is reflected in the relative intensity ratio of the VOC₃H₅⁺ peak as can be seen by comparing Figs 3a and b.

On the surfaces which adsorb propene, additional peaks, identified as VOH^+ , VOH_2^+ , VO_2H^+ and $VO_2H_2^+$ are found, indicating that the αH is abstracted at the catalyst surface and remains on the surface under the conditions of the performance of the adsorption.



Fig. 3. a: SIMS spectrum of a partially [oxygen covered $V_6O_{13}(001)$ surface after propene adsorption, b: SIMS spectrum of an oxygen free $V_6O_{13}(001)$ surface after propene adsorption

Conclusion

The adsorption study confirms that adsorption only takes place if V^{4+} ions are present on the surface. It could also be established that the adsorption of propene occurs in the allylic form and that hydrogen is abstracted on the catalyst surface.

General conclusion

As a general conclusion of this work a model for the catalytic oxidation of propene to acrolein is proposed confirming the generally accepted model for the oxidation of propene to acrolein on transition metal oxides.

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APPLIED HETEROGENEOUS CATALYSIS AND CATALYTIC ENGINEERING AS A RESEARCH ACTIVITY OF THE APPLIED CHEMISTRY GROUP AT LIÈGE UNIVERSITY*

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A brief report is given on the main research activities of the Applied Chemistry Group at the Institute of Industrial Chemistry of Liège University. It covers the following fields: industrial chemistry (chemical, petrochemical and polymerization processes), chemical engineering (chemical reaction engineering, applied physical chemistry, heterogeneous catalysis) and mathematical methods applied to chemical engineering (simulation, optimization, dynamics and control of chemical systems).

The activity of the Group of Applied Chemistry (GAC) is focussed on two main topics:

 the development of new processes and new products or any combination of both giving an answer to the actual anxious search of partial alternatives to petrochemistry;

- the use of continuous 3-phase catalytic systems which are the speciality of the Group and whose knowledge allows to overcome the complexity of most of the reactions mentioned hereafter.

a. The problems which are actually set to the economic and industrial world are becoming more and more worrying: should the traditional raw materials, natural gas and oil, remain still available and at what price?

By studying the processing of alternative or complementary raw materials for the production of chemicals, the GAC tries to give answers to these questions.

The raw materials used are renewable and broadly available in our countries. Moreover, this assures the independency what the supplies concern.

The new products studied concern sectors like food and drugs. The acceptation criteria in these fields are very severe. The processes leading to their manufacture are then necessarily of great complexity: at the reaction level (processing of multiphase systems) and at the technical level (allowing high quality).

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b. Three-phase catalysis may be considered as one of the most complex step of industrial processes. The productions which have just been evoked, mostly belong to the three phase systems. The GAC includes a team whose works on the use of these systems, specially in continuous tricle-bed reactors, are of some reputation.

The trickle-beds are largely used in the oil-refining industry. The GAC has enlarged their applications to the manufacture of fine chemicals. The amount of reactants treated is naturally far lower in the second case. For an application to an other scale and to other products, this has required the adaptation of the parameters used in hydrotreatment and a better understanding of the operation and control of this kind of reactors. Providing this, one can benefit of the inherent advantages of the trickle-bed reactors. It can be easily understood that these advantages are the ones which allow to satisfy the severe specifications of fine chemicals. Indeed, the plug-like flow diminishes the dispersion and leads to high conversions. The low liquid-solid ratio minimizes the possible side reactions taking place in homogeneous phase.

These two advantages contribute to reach the great purity of the products sometimes without any purification.

Since 1974, the Department of Industrial Chemistry is interested in carbohydrate processing. These are indeed issued from natural and renewable sources which are moreover broadly available in our country. So comes xylose from the degradation of the hemicellulose components of woody plants, corn cobs and straw. Glucose and fructose are obtained by acid hydrolysis of the saccharose coming, in our country, from sugar beet. Maltose as well as glucose are produced from the hydrolysis of starch. Concerning lactose, it is present in the milk of all mammals at 2-8% concentrations.

It is produced from whey separated from its proteins. It is actually available in great quantities but has a very small market. Processing of these different raw materials leads to a number of valuable products.

Our laboratory does specially study the following treatments: selective hydrogenation in order to get fine or very pure chemicals, oxidation by catalytic as well as by enzymatic processes, and hydrogenolysis which is an alternative route for manufacturing some products like glycerol by direct non petrochemical way.

Hydrogenation of carbohydrates

The products obtained by carbohydrate hydrogenation seem actually to have good market perspectives if they can be produced sufficient purity (with a minimum refining steps). Moreover, for sorbitol production, the capacity of current plants is high enough to make a continuous process desirable. All these reasons suggested to our laboratory team to apply the trickle-bed technology to these productions. Moreover, this allows to use a more expensive catalyst which would not support the high losses encountered in batch processing. This is the reason why we perform all our studies on ruthenium catalyst which is much more active than the well known Raney nickel catalyst. This was possible because we developed a patented reactivation procedure which allows the ruthenium catalyst to exhibit a life of reasonable length.

The combination of these two advantages (reactor leading to higher selectivity and more active catalyst) enables our laboratory to define a broad program of research.

We first started in demonstrating the already mentioned advantages of trickle-bed reactors on stirred tank reactors by running many comparison experiments. Then we developed an *isothermal* micro tricle-bed reactor of 7 mm in diameter without any mass or heat transfer limitations in order to study the hydrogenation reactions in such an installation.

We showed that this was suitable for kinetic studies and determined the optimum operating conditions for the hydrogenation of glucose and maltose into sorbitol and maltitol, respectively. We then were ready to switch to a larger scale closer to the industrial conditions.

We are now studying the behaviour of an *adiabatic* completely automated trickle-bed reactor of 19 mm in diameter and 4 m in length. The results we got are encouraging and allow any scale up. We are now on the point to build a pilot plant for these reactions. So, this is an example of a 5 years study which has encountered all the problems of a process developing from the kinetic studies to the scale up included the special designs requested for running medium pressure vessels.

This research has shown the interest of using the trickle-bed technique for carbohydrate hydrogenation. During this time we studied:

- the production of high purity sorbitol which is largely used in pharmacy, cosmetics, alimentation and industrial surfactants;

- the production of food grade maltitol for medical purposes and diet;

- the maximization of the mannitol-sorbitol ratio, both produced from fructose. Mannitol, which is specially produced by this way, has an extended use in the confection of tablets in drugs;

- the definition of purity requirements of lactose before hydrogenation.

Lactitol seems to have good perspectives as far as its fatty esters have recently shown specific detergent properties.

Our knowledge of the saturation of the C=O double bond in carbohydrates has led us to develop techniques for the transformation of ketone into secondary alcohol. We have focussed our attention on the activation and deactivation of supported ruthenium catalysts for this specific reaction.

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Hydrogenolysis of carbohydrates

The hydrolysis of cellulose and hemicellulose glucose and xylose, respectively, is well known. Our purpose is to convert these 5- and 6-carbon molecules into smaller ones. Glycol and glycerol are preferred to hydrocarbons because they are more valuable. Since 1979, we studied the possibility of glycerol production by this way in sufficient amounts and purity. The experiments are conducted in two agitated slurry reactors. They allow to work at 250 degrees and 250 bar. The influence of the different variables is studied and good perspectives are suspected. The study of carbohydrate hydrolysis implies numerous analysis facilities. For this purpose, two automated liquid chromatographs, one gas chromatograph directly connected to the installation (both belonging to the Department) and one gas chromatograph connected with a mass spectrometer are used.

Oxidation of glucose

Gluconic acid and particularly its gluconate salts are of interest as sequestrant used in pharmacy and in industrial cleaning. But what specially has interested us in this reaction, is that it can be performed by classical catalysis as well as enzymatic catalysis. This is a good opportunity to compare the use of a trickle-bed reactor with chemical and biological catalysts. The information and analogy that should be obtained could be an open door to biotechnology and supported enzyme processing which is actually broadly recognized as a field of important development.

Valorization of woolwax

Woolwax is an important by-product of crude wool washing. The potential applications of this product are numerous (e.g. in cosmetic and pharmaceutic industries, synthesis of fatty alcohols, . . .) but often restricted by the presence of poisons like sulfur compounds. A research of our group in this field is the development of a hydrodesulfurization process of woolwax in a trickle-bed reactor. This reaction is presently checked in a high pressure fully automatized trickle-bed reactor.

We have seen how the Department is studying the valorization of natural raw materials. It is also active in other fields and we would like to mention other researches done in our laboratories.

Hydrotreating of heavy petroleum fractions and liquefied coal

During the past years, the hydrotreating processes of heavy petroleum fractions became more and more important economically. At present, about 40 percent of the total amount of the oil produced in the world is hydrotreated, *i.e.*, roughly 1 billion of tons per year. Furthermore, the direct liquefaction of coal will yield in the future a large amount of a heavy oil containing sulfur, nitrogen and heavy metals, requiring thus another hydrotreating process.

In the frame of our research concerning these hydrotreating processes, we have adopted two main working orientations. The first one consists in developing a new non conventional catalyst for the demetallization. The conventional hydrodesulfurization catalysts — containing group VI — group VII metal oxides — are relatively rapidly deactivated by coke and metal sulfur deposits.

Due to the relatively high price of these elaborated of these catalysts, it is often necessary to use a guard reactor containing a cheaper catalyst with a high adsorption capacity to remove a large amount of metal (Ni, V).

We are now developing such a catalyst based on polymetallic ocean nodules which seems to have a good demetallization capacity. These nodules have a relatively low price because they may be used by metallurgical industries after their utilization as catalyst. This catalyst is currently checked in a fully automatized laboratory scale tricle-bed reactor, working at high temperature and pressure and processing heavy oil distillates and residues.

Our second research orientation in this hydrotreating field consists in improving the design of the reactors in which this process is generally achieved, *i.e.*, the trickle-bed reactors. In such reactors, the gas and liquid flows are completely heterogeneous leading to a relatively poor gas-liquid-solid contact.

In order to improve this contact by a proper reactor design, we have started, a few years ago, to develop a hydrodynamic model describing analytically the heterogeneous nature of the fluid flows.

This model, based on a stochastic description of both fluid flows and packing, has been successfully applied in the simulation of laboratory scale trickle-bed reactors processing various reactants. At present, we are analysing the scale-up problems in a large scale flow model (e.g. the liquid distributor effects).

Valorization of gasified coal

One of the most interesting way to gasify coal in Europe is the underground coal gasification by an oxygen-steam mixture. Our group participates in a research concerning this type of gasification within the framework of the Belgian-German project for U.C.G. at great depth (I.D.G.S.T.). One of its main contribution is the development of a chemical engineering methodology for the modelling of the various kinetic processes (mass and heat transfers) occurring in the gasifier. From of more "catalytic" point of view, our group is now developing new catalysts for the shift reaction in order to adjust the CO/H_2 ratio in the gas.

This reaction is generally realized under such a condition when the equilibrium is nearly reached. Thus the conversion of carbon monoxide into hydrogen is facilitated by low temperature operations. That is the reason why the old high temperature catalysts containing iron oxides are presently replaced by low temperature catalysts containing copper oxide. Unfortunately, these catalysts are very sulfur sensitive.

That is the reason why new low temperature catalysts are now under development which would resist to small amount of sulfur compounds (e.g. 1% of H₂S).

The best solutions reported in the literature seem to be a Co-Mo-K or a Co-Mo-Li mixture. The contribution of our group consists in developing catalysts with similar properties but containing cheaper metals than Co or Mo.

This reaction is continuously performed in a so-called BERTY reactor, stirred with turbine. It is on line connected to a gas chromatograph. The installation is completely equipped for controlling and regulating all the variables of the process. This is managed in real time by a micro-computer which automatically orders the analysis of the products and decides to command the regulation loops. The final data acquisition is only realized when the variables are tested to be meaningly stable. So can the computer perform alone a complete "experimental plan" and record all the data. These data may then be transferred to a bigger computer for further processing and specially for parametric identification. The direct connection between the two computers will also be studied.

This micro-computer installation is generally designed and may serve to develop other computer systems for managing other reactions.

Desulfurization of industrial sulfur containing light gases

Our purpose is to study the adsorption of sulfur compounds (H_2S , COS, mercaptan) on several solid catalysts. The study is conducted in a continuous fixed bed reactor. The installation is designed for automatic control and automatic sampling and analysis.

We determined by this way the optimum operating conditions for various zinc oxide catalysts.

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Characterization of catalyst structure

When developing a new process based on self-made or commercial catalysts, it is often useful to characterize the various types of checked catalysts.

To do this, we developed various techniques and methods, which are, essentially:

- determination of polosity, pore size distribution by Hg porosimetry (macropores), and adsorption and desorption isotherms (micropores);

- kinetics and thermodynamics of gas vapor and liquid, adsorption onto adsorbents;

- thermogravimetric study of catalyst particles (e.g. various oxidation levels of Ru supported catalysts);

- a detailed interpretation of adsorption desorption isotherms (B.E.T. methods).

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SELF-INHIBITION BY RESIDUAL HYDROGEN RETAINED IN CATALYSTS*

(SHORT COMMUNICATION)

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In a recent study of the stoichiometry of O_2-H_2 titrations on supported platinum catalysts, PRASAD et al. [1] found that no consistent stoichiometry was observed when the chemisorption values for O_2 and H_2 were obtained from measurements on freshly reduced catalyst surfaces; a few O_2-H_2 cycles at room temperature, however, smooth out or "homogenize" the surface to give reproducible results in the titrations.

To investigate why a freshly reduced $Pt-Al_2O_3$ catalyst surface is often not reliable or reproducible in gas titrations, the effect of the reduction temperature itself on the properties of the catalyst was first studied. The techniques employed were catalytic activity studies, chemisorption of H_2 on the catalyst and temperature-programmed desorption of H_2 from it. The main results of this study (MENON and FROMENT [2]) are:

1. Reduction of $Pt-Al_2O_3$ catalysts in H_2 at increasing temperatures in the range 450-600 °C has a strong attenuating effect on hydrogenolysis of *n*-pentane and *n*-hexane at 300-400 °C. The catalyst can be restored to its original activity by air oxidation at 500 °C, followed by reduction at 400 °C. This shows the reversibility of the attenuation and the absence of sintering or permanent structural changes of the catalyst.

2. The attenuation of hydrogenolysis caused by high temperature H_2 is similar to that produced on chloriding or mild sulfiding of the catalyst.

3. It is the stronger chemisorption of H_2 at higher temperatures (possibly involving the sub-surface layers of Pt as well) which renders a fraction of the surface Pt atoms so unreactive that they cannot react any more with H_2 or O_2 during surface titrations at 20 °C or with the paraffins at 300-400 °C.

4. The profuse desorption of H_2 from the catalyst in the range of 50– 300 °C during TPD is an indication of the strong hydrogenolysis activity of

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the catalyst. The Pt sites responsible for the hydrogenolysis seem to be those which also get attenuated by the stronger chemisorption of H_2 .

Similar results have also been obtained for $Pt-SiO_2$, $Pt-TiO_2$ and platinum black (MENON and FROMENT [3]).

The above results are in broad agreement with those obtained [4], in recent years by TÉTÉNYI, PAÁL, GUCZI, NAGY, ENGELHARDT and others at the Institute of Isotopes and Central Research Institute for Chemistry of the Hungarian Academy of Sciences, emphasizing the importance of residual hydrogen retained in catalysts. Self-inhibition of catalytic activity by such residual hydrogen seems to be a general phenomenon occurring in the case of supported metallic catalysts and even oxide catalysts. Its unsuspected presence may perhaps have vitiated some of the pioneering work in the field of catalysis.

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CHAIN LENGTHENING IN METAL-HYDROCARBON SYSTEMS*

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In our paper we presented evidences for the chain lengthening activity of transition metals, which seems to be a general phenomenon under conditions of "deep" fragmentation. The chain lengthening of hydrocarbons in a metal-hydrogen-carbon heterogeneous system supports the recent suggestions that incorporation of surface carbon into hydrocarbons during Fischer-Tropsch synthesis may take place via oxygen-free CH_x species. The experimental results in the present study and in Ref. [9, 10] emphasize that the formation of trace amount of isomers under hydrogen deficient conditions as well as the apparent methylpentanes \rightarrow benzene transformation can be interpreted by C_1 insertion- C_1 abstraction mechanism.

Introduction

Interaction of saturated hydrocarbons with metal surface in the presence of hydrogen leads to the rupture of the C-C bond at elevated temperatures. It has been established, that the hydrogen/hydrocarbon ratio plays an important role in the formation of product distribution pattern. Thus, in large excess of hydrogen only single C-C bond rupture occurs and the product distribution pattern is characteristic to the metal investigated. For example, on Ni catalysts under such condition terminal splitting [1-3] of the C-C bond can be observed (α -splitting), whereas on Pt catalysts the C-C bond rupture is more or less statistical [4, 5] depending on the structure of the hydrocarbon, dispersion, alloying, *etc.* At low hydrogen/hydrocarbon ratios, however, deep fragmentation prevails [2, 3, 6] resulting in selective formation of methane and poisoning of the catalysts. Using ¹⁴C intermediate tracing [2, 3, 6] we have already demonstrated, that in the absence of hydrogen the rate of desorption of intermediate products is considerably slower than that of the C-C bond rupture on the surface.

In the present paper we wish to summarize experimental data concerning chain lengthening in metal-hydrocarbon systems obtained in our laboratory.

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Free energy changes (ΔF) of n-pentane \rightarrow n-hexane transformations at 600 K

Reaction	ΔF , kJ mol ⁻¹
a) $CH_4 + C_5H_{12} = C_6H_{14} + H_2$	61.7
b) $2 C_5 H_{12} = C_6 H_{14} + C_4 H_{10}$	0.4
c) 2 $C_5H_{12} + 3 H_2 = C_6H_{14} + 4 CH_4$	-19.5

In Table I the free energy change (ΔF) for various hypothetical *n*-pentane \rightarrow *n*-hexane transformations is presented. As shown by data in Table I reaction *a*, *i.e.* addition of methane to pentane, is thermodynamically unfavourable, whereas the hydrocarbon "setting up" might proceed if the reaction is accompanied by "deep" fragmentation of *n*-pentane (see for example reaction *c*). It is important to note, however, that the reactivity of hydrocarbons in hydrogenolysis generally increases with increasing molecular weight, that is, the

Catalyst*	$wt\%/SiO_2$	F/BET m ² /g ^{-,}	$^{V_{\mathrm{H}_{2}}}_{\mathrm{mL}\ \mathrm{g}_{\mathrm{cat}}^{-1}}$	D %	d_{s} nm	$d_{ abla}$ nm
0.3-Ni-B		2.5		0.3	270	50
).9-Ni-B		6.2		0.9	110	25
16-Ni-Imp	15		4.1	16	6.7	5.7
27-Ni-Dep	13.3		6.6	27	3.7	
46-Ni-Dep	13.3		11.1	46	2.2	
9.5-Ru-Imp	5		1.2	9.5		
Ru-B		6.7				15
Rh-B		2.5				20
Pd-B		2.2				
Re-B		6.5				10.5
Os-B		2.3				
11-Os-Imp	3		0.44	11	9.1	6.7
Ir-B	7.4					
Pt-B	4.3					10
4-Pt-Exch	1.5		0.39	44	5.4	3.6
Cu-Ni-Imp	2.5 - 2.5		0.08			
Au-Ni-Imp	2.5 - 2.5		0.13			

Table II

* The initial number is the dispersion as measured by hydrogen chemisorption; B, Exch, Imp and Dep, respectively, indicate metal black, preparation by ion exchange, impregnation and deposition.

probability of chain lengthening must be strongly dependent on kinetic conditions.

The first systematic studies on homologation of saturated hydrocarbons have been performed by O'DONOHOE, CLARKE and ROONEY [7, 8] with W, Rh, Pd, Mo, Nb films. Our recent paper deals with the homologation activity of Ni catalysts and of Group VIIIb transition metals (Ni, Co, Ru, Rh, Pd, Os, Ir, Pt), and from Group VII Re. Discussion of the observed results may give deeper insight into the catalytic behaviour of transition metals in hydrocarbon transformations under hydrogen deficient conditions. Some of our results has already been published in Refs [9, 10].

Experimental

All catalytic measurements have been performed in a glass made circulating system volume of 0.132 L connected *via* a sampling valve to a Packard 424 gas chromatograph. The products were analysed either with a capillary column (50 m) filled with squalane at 323 K or, in order to diminish the time of the analysis, with a 6 m long column with squalane on chromosorb P at 343 K.

Supported noble metal catalysts were prepared by impregnation using water soluble chlorine compounds. In order to avoid support effects metal blacks were prepared, too. Method of preparation has already been published [11]. Characterization of the catalysts is in Table II. The number of active metallic sites was determined from hydrogen adsorption isotherm measured in the 0.1-1 mbar pressure range at 295 K. Surface area of metal blacks was inferred from BET/N₂ measurements. Value of the average particle size (d_s) assuming spherical particles as well as the main crystallite size obtained from X-ray diffraction data (d_v) are listed in Table II, too.

Results and Discussion

Reactivity of hydrocarbons in chain lengthening

Formation of products on 0.9-Ni-B, 46-Ni-Dep and Cu-Ni-Imp (2.5 wt% each) catalysts as a function of time is depicted in Figs 1a, b and c, respectively. It has generally been observed that the rate of formation of hydrocarbon fragments slows down with time indicating that the catalyst surface is covered by carbonaceous deposits at the very beginning of the metal-hydrocarbon interaction. Further on we report upon the initial product distribution patterns measured at 1-5% conversions (at 2-5 minutes contact time) as well as upon the maximum rate of formation of hydrocarbons with higher carbon number than the parent one. Results are summarized in Table III.

In Fig. 2 we summarized data on the selectivity of chain lengthening measured on 46-Ni-Dept at 613 K using normal paraffins. As shown on Fig. 2 the probability of chain lengthening increases with increasing carbon number in agreement with thermodynamic expectations. We did not observe homologues formation with propane in the temperature range 523-663 K. From *n*-butane *n*-pentane, *n*-pentene and trace amount of 2-methylbutane were

Table 1II

Product

Catalyst	Hydrocarbon	$p_{ m HC}/p_{ m H_2}$	T/\mathbf{K}	C ₁	C ₂	C ₃	C,
46-Ni-Dep	Propane	1.5	613	67	23		
	n-Butane	1.5	615	43.5	32	13.5	9.7
	n-Pentane	1.5	613	50.1	24.6	6.3	7.5
	<i>n</i> -Hexane	1.5	613	45.3	13	4.9	2.3
	n-Heptane	1.5	613	33.2	14.2	7.4	2.9
6-Ni-Imp	n-Pentane	1.5	623	63.0	17.3	6.5	3.5
P	c-Pentane	1.5	623	61.5	10.1	7.7	5.3
	2.2-Dimethylpropane	1.5	620	62.5	14.3	18.5	5.1
	2.3-Dimethylbutane	1.5	625	75.4	10.4	6.7	4.3
	2.2-Dimethylbutane	1.5	623	66.5	8.7	14.3	6.8
	2-Methylpentane	1.5	625	66.2	6.3	4.7	3.2
	3-Methylpentane	1.5	620	63.5	7.4	6.3	6.1
	Methylcyclopentane	2	623	53.5	6.3	4.6	4.3
	2-Methylpentane	2	583	52.7	12.1	6.3	4.8
	3-Methylpentane	2	583	55.7	15.3	5.8	6.2
Ni-Cu/SiO ₂	c-Pentane	2	613	21.2	18.6	13.9	14.2
Ni-Au/SiO ₂	c-Pentane	2	613	17.4	14.3	22.7	16.1
).9-Ni-B	n-Pentane	1	573	84.1	5.7	3.6	4.8
	c-Pentane	1	573	80.2	5.7	2.4	3.2
6-Ni-Imp	<i>n</i> -Pentane	1	573	81.4	6.3	2.4	3.6
	c-Pentane	1	573	74.6	5.5	2.6	4.3
27-Ni-Dep	n-Pentane	1	573	66.5	16.8	4.3	3.6
	c-Pentane	1	573	52.3	10.2	13.6	2.2
6-Ni-Dep	n-Pentane	1	570	60.6	14.2	3.2	2.1
	c-Pentane	1	570	53.8	10.7	3.6	4.3
Co-B	n-Pentane	2	623	76.9	12.3	3.2	1.3
Ru-B	n-Pentane	2	623	60.3	13.1	8.6	10.2
Rh-B	n-Pentane	2	623	63.9	16.5	4.7	6.3
$Pd-B^b$	n-Pentane	2	623	47.2	6.3	7.4	8.2
Re-B	n-Pentane	2	623	88.2	5.5	3.6	1.6
l1-Os-Imp	n-Pentane	2	623	83.2	6.7	4.7	2.8
Os-B	n-Pentane	2	623	82.5	10.2	2.4	1.1
Ir-B	n-Pentane	2	623	57.8	16.6	9.2	8.3
$Pt-B^{c}$	n-Pentane	2	623	26.6	6.3	8.2	6.4
44-Pt-Exch ^d	n-Pentane	2	623	22.0	23	11.1	8.5
$^{a}R_{H} = 1$ $^{b}28.2\%$ $^{o}40.7\%$	tate of formation of homo pentenes; pentenes, 5.1% cyclopen	blogues (C_n tene;	+1) in me	ol m^{-2} (1	met) s ⁻¹	;	

distributions

$i \mathbf{C}_5'$	nC_5	2MP	3 MP	2MH	МСР	В	T	X	$R_{\mathrm{H}}^{\mathrm{a}}$
_	7	_		_	_	-	_	_	
tr	1.3^{e}								$2.3 imes 10^{-11}$
-	—	2.1	-	-	-	9.5	2.3		$6.3 imes 10^{-8}$
1.5	4.3	0.7	-	tr	-	10.2	14.5	3.3	$6.2 imes 10^{-8}$
-	-	-	_	_	_	20.2	16.6	5.5	6.6×10^{-8}
1.2	-	0.7	-		-	5.5	2.3	-	$1.1 imes 10^{-8}$
1.4	-	0.8	-	-		9.5	3.7	tr	$2.7 imes10^{-8}$
-	-	-	-		_	-	-	-	
3.2			tr	-	-	tr	-	-	
3.7		tr	-	_	-	tr	-	-	-
2.8	-	-	-	tr	_	6.7	10.1	-	$6.3 imes 10^{-8}$
1.2	2.8	-	-	_	-	3.6	9.1	-	$4.7 imes10^{-8}$
1.3	0.6	3.3	2.1	1.1	-	8.5	12.3	2.1	$9.6 imes10^{-8}$
1.6	2.7	-	-	-	-	5.2	14.6	-	$1.2 imes 10^{-8}$
3.2	0.1	—	-	_	_	3.6	10.1		$9.6 imes 10^{-9}$
_	20.1				6.3	5.7	-	-	$1.3 imes10^{-9}$
	18.3	tr	tr		3.7	6.2	1.3		$1.4 imes 10^{-9}$
0.1	-	tr	-			1.7	-	_	$7.2 imes 10^{-10}$
0.2	2.9	0.2	-	-	-	5.2	_	-	$3.6 imes 10^{-9}$
0.1	_	0.1	-	-	-	6.1	-		$7.7 imes 10^{-9}$
0.2	3.6	0.1	-	-	-	7.8	1.3		$1.2 imes 10^{-8}$
	-	-	-	-	-	8.7	0.1		$1.1 imes 10^{-8}$
0.6	7.7	0.1	-	-	-	11.2	2.1		$2.8 imes 10^{-8}$
1.1	-	2.2	_	-	-	15.5	1.1		$3.6 imes 10^{-8}$
0.1	1.9	0.6				19.5	5.5		$7.4 imes 10^{-8}$
_		-				6.3	-		9.6×10 ⁻¹⁰
1.5	-	0.3				4.7	1.3		$8.3 imes 10^{-9}$
0.6		0.2				7.8	tr		$1.6 imes 10^{-8}$
2.1	-	-				0.6	_		$2.6 imes 10^{-11}$
-	-	-				1.1	-		1.52×10^{-9}
_	-	-				2.6	_		$1.2 imes 10^{-8}$
-	-					3.8	_		$3.3 imes 10^{-9}$
1.5	-	-				6.6	_		$5.2 imes 10^{-10}$
6.5	_				-	0.2	_		1.1×10^{-12}
4.3	-	-				0.7			$2.3 imes 10^{-11}$
	1								

 $^{\rm d}$ 4.6 pentenes, 11.8 cyclopentene; $^{\rm e}$ 0.1% pentene



Fig. 1. Transformation of cyclopentane at 623 K on 46-Ni-Dep, (a); 0.9-Ni-B, (b) and Cu-Ni-Imp, (c) catalysts. (1) — methane; (2) — ethane; (3) — propane + butane; (4) — benzene; (5) — toluene; (6) — methylcyclopentane



Fig. 2. Percentage of C_{n+1} products (distribution expressed in terms of carbon number) in homologation of normal paraffins on 46-Ni-Dep catalyst ($p_{HC}/p_{H_2} = 1.5$, T = 613 K)

formed. *n*-Pentane and *n*-hexane resulted mainly in the formation of benzene and toluene. For heptane the selectivity of homologues formation is less than that for *n*-pentane and *n*-hexane owing to the demethylation of xylenes at 613 K.

The sensitivity of chain lengthening for the structure of the starting hydrocarbon is demonstrated in Fig. 3 using various pentane and hexane

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Fig. 3. Effect of the hydrocarbon structure upon formation of C_{n+1} products (catalyst 16-Ni -Imp, T = 623 K, $p_{HC}/p_{H_2} = 1.5$)

isomers. *n*-Pentane, cyclopentane, 2-methylpentane and 3-methylpentane yield mainly benzene and toluene. 2,2-Dimethylpropane, 2,3-dimethylbutane and 2,2-dimethylbutane were inactive in the homologue formation. The mechanism of chain lengthening could be verified on the basis of the above observations. Among the homologues the C_{n+1} products in the case of 2,2-dimethylpropane, 2,3-dimethylbutane and 2,2-dimethylbutane confirms that the chain lengthening does not take place simply by alkyl or carbene recombinations.

In Scheme 1 the proposed mechanism is depicted. According to the mechanism the key step is the carbene insertion into terminal olefin via metallo-



cyclobutane formation. On Ni catalysts carbene insertion is readily followed by 1,6-cyclization resulting in the formation of aromatics. As far as 2,3-dimethylbutane and 2,2-dimethylbutane is concerned the absence of any C_7 hydrocarbons may be interpreted by steric reasons. As shown in Fig. 3 2-methylpentane yields more toluene than 3-methylpentane although in the latter hydrocarbon the probability of formation of a vinyl group is greater. All these evidences confirm that chain lengthening is a highly sensitive reaction for steric and/or electronic factors. The selectivity and the rate of formation of benzene is larger with cyclopentane than that with *n*-pentane. This difference in reactivity and selectivity seems to prove that ring opening on carbon poisoned catalyst results in the formation of terminal olefin. Returning to the problem of product distribution pattern from both *n*-pentane and cyclopentane small amount of branched hydrocarbons are formed as well. The 2-methylpentane/benzene ratio was 1.5×10^{-2} and 2.3×10^{-1} at 603 K on Ni-B and 46-Ni-Dep, respectively. No



Fig. 4. Rate of benzene formation (R_B) and of fragmentation (R_H) with *n*-pentane at 573 K on 16-Ni-Imp (circles) and 0.9-Ni-B (squares)



Fig. 5. Partial pressure of benzene (1), toluene (2) and of fragments at 2 minutes contact time on 46-Ni-Dep, T = 603 K, $p_{\rm HC} = 2.66$ kNm⁻²

traces of 3-methylpentane or methylcyclopentane can be observed suggesting that internal double bond is inaccessible to carbene insertion on Ni catalyst.

 $\rm Ni-Cu/SiO_2$ and $\rm Ni-Au/SiO_2$ bimetallic catalysts behaved, however, in a different way. On these catalysts benzene and methylcyclopentane appeared in commensurable quantity. On $\rm Ni-Au/SiO_2$ traces of 2-methylpentane and 3-methylpentane could be detected as well. The origin of methylcyclopentane is still under discussion.

Kinetic results

The rate of formation of products has been given in Figs 4 and 5 as a function of hydrogen pressure for n-pentane at 573 K and for 2-methylpentane at 603 K, respectively. As revealed by Figs 4 and 5 the reaction order with respect to hydrogen is positive for fragmentation in the pressure range of hydrogen investigated whereas the rate of hydrocarbon "building up" i.e. formation of benzene and toluene passes through a maximum of 1:2 hydrocarbon/hydrogen ratio. Such volcano shaped kinetic curves have been generally observed in hydrocarbon transformations [12]. In our case the following explanations can be given. The right side of the curve can be interpreted by the low concentration of carbene and olefin on the surface. Chemisorption measurements with H_{α}/n -butane mixtures have confirmed that the surface coverage of hydrocarbon decreases sharply with increasing H₂/n-butane ratio. The positive reaction order of fragmentation indicates that hydrogen sweeps hydrocarbon species off the surface. As far as the left side of the volcano shaped curve is concerned one has to consider that in the absence of hydrogen both intermediates *i.e.* carbene and olefin may be deactivated by loosing hydrogen, thereby giving rise to the decrease of the working active sites.

The reaction order with respect to hydrocarbon, b, has also been determined at 603 K. These data are summarized in Table IV. The value of b is positive but considerably less than unity for both fragmentation and chain

HC	Catalyst	T/\mathbf{K}	<i>b</i> ₁ *	<i>b</i> ₂ **
nP	46-Ni-Dep	603	0.33	0.52
2MP	46-Ni-Dep	603	0.23	0.48
nP	Ni-B	603	0.25	0.36
2MP	Ni-B	603	0.13	0.33
2MP	Ni-B	633	0.07	0.19

Table IV

Reaction order with respect to hydrocarbon in homologation

* b_1 - hydrocarbon order of fragmentation.

** $b_2 - hydrocarbon$ order of chain lengthening.

lengthening suggesting that the catalyst surface is covered mainly by hydrocarbon owing to the low excess of hydrogen and to the high reaction temperature.

The apparent activation energies are 17-32 and 88-105 kJ mol⁻¹ for benzene formation and fragmentation, respectively, from *n*-pentane in the temperature range 550-600 K with 46-Ni-Dep catalysts. With 2-methylpentane with the same catalyst the activation energies are 15-25 and 75-85kJ mol⁻¹ for toluene formation and fragmentation. The apparent activation energy of the formation of benzene becomes negative above 653 K. At such high temperatures the rate of desorption of benzene (toluene) and its fragmentation on the surface becomes commensurable owing to the larger activation energy of the latter process.

Effect of dispersion of Ni catalysts upon chain lengthening

Figure 6 shows the selectivity and the rate of benzene formation (in brackets) from *n*-pentane on Ni catalysts of various dispersion. Apparently the crystallite size of Ni influences the probability of chain lengthening to certain extent; it increases with decreasing crystallite size. This observation may emphasize the importance of surface sites of low coordination *i.e.* edges, kinks, corners *etc.* in carbene insertion. The shape of the kinetic curves (compare Fig. 1a and 1b) puts the matter, however, in another light. With Ni-B



Fig. 6. Percentage of C_{n+1} products and rate of their formation on various Ni catalysts at 573 K, $p_{\rm HC}/p_{\rm H_2} = 1$

Catalyst	не		TUV	C/Ni _s		
Catalyst	нс	PHC/PH ₂	1/K	A*	в	
0.9-Ni-B	$c\mathbf{P}$	2	603	3.98	3.47	
0.9-Ni-B	$c\mathbf{P}$	2	643	9.22	7.15	
0.9-Ni-B	$n\mathbf{P}$	2	603	4.86	4.03	
46-Ni-Dep	$c\mathbf{P}$	1.5	633	0.67	0.33	
46-Ni-Dep	$c\mathbf{P}$	2.5	603	0.38	0.33	
46-Ni-Dep	cP	0.04	602	0.03	0.04	

 Table V

 C/Nis ratio after 60 minutes contact time

 $^*\,p_{\rm HC}=53.2$ mbar; A - sample oxidized at 773 K and CO_2 measured; B - sample hydrogenated at 773 K and CH_4 measured.

catalysts the rate of benzene formation drops rapidly indicating that carbonaceous deposits are accumulated on the surface blocking the active sites. Analysis of carbon content of working catalysts has confirmed our suspicion. The value of the number of carbon atom per surface Ni atoms, C/Ni_s, is presented in Table IV. After 60 minutes contact time the amount of carbon on Ni-B is equivalent to 3–5 monolayers depending on the experimental conditions. 46-Ni-Dep catalysts seems to be more resistant to carbon poisoning. Oxidative treatment gives larger values for C/Ni_s than the reductive one pointing to the fact that part of the carbonaceous deposits is in graphite form.



Fig. 7. Temperature programmed hydrogenation of carbon deposit from 0.9-Ni-B catalyst. T = 593 K; (1), C/Ni_s = 0.8; (2), C/Ni_s = 1.5; (3), C/Ni_s = 3.7



Fig. 8. Position of peak temperatures as a function of carburation temperature (T_r) ; (1) α form; (2) β form; (3) γ form

The reactivity of surface carbon deposits has been investigated in more detail by temperature programmed hydrodesorption (TPHD) measurements. In these experiments the surface carbon was formed from ethylene at different reaction temperatures (T_r) . Figure 7 shows a typical TPHD measurement revaling different surface structures of carbon. Position of the peak temperature (T_p) is shifted to higher temperatures with increasing carburation temperature (T_r) as depicted in Fig. 8. The dispersion does only slightly influence the position of the peaks at elevated temperatures, but there is considerable difference in the amount of the various forms of carbon on these samples.

Table	VI	
-------	----	--

Cataluat	TIK	Distribution, %					
Catalyst	1 ₇ /K	α"	$\alpha + \beta$	γ	δ*		
0.3-Ni-B	623	0.9	52.6	34.3	12.5		
	723	—	11.3	43.0	44.7		
0.9-Ni-B	623	1.0	58.1	30.6	10.3		
16-Ni-Imp	633	3.3	45.1	46.5	5.1		
	723	1.5	39.4	48.6	10.5		
46-Ni-Dep	623	5.6	37.4	45.8	1.2		
	723	2.9	32.1	64.7	3.3		

Composition of carbon deposits as measured by TPHD, $C/Ni_s = 3.3 - 4.2$

* Calculated from carbon balance.

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According to the data in Table VI at 623 K on Ni-B catalyst part of the carbon deposits can be found in the highly unreactive δ form, whereas on the more dispersed catalysts α', α, β and γ forms are dominated. Apparently the stability of the more reactive forms is larger on small crystallites even in the absence of hydrogen. On the basis of the above presented observations we may safely propose that amorphous (γ) and graphitic (δ) carbon is inactive in the course of chain lenghtening, whereas α and β forms might serve hypothetically as a source of carbone.

Activity of transition metals in chain lengthening

The chain lengthening activity of VIIIb metals and Re has been tested by measuring the rate of formation of benzene from *n*-pentane with blacks at 623 K using a 2 : 1 hydrogen/hydrocarbon mixture. The experimental results are depicted in Fig. 9 together with the ethane hydrogenolysis activity of these metals [23] at 523 K (H₂/HC = 10). In both the second and third rows the rate of benzene formation increases moving from right to left. Similar results were obtained with silica supported metals. At 623 K both Pd and Pt blacks yield only small amount of C_{n+1} products. The low activity of these metals can be interpreted in terms of their poor carbene formation activity since selfpoisoning influences only slightly the formation of olefins. The presented data in Fig. 9 reveal that the hydrogenolysis and chain lengthening activity show remarkable parallelism over these metals. Taking into account that chain



Fig. 9. Rate of benzene formation $(w_{\text{hom}}, \text{ mole } \text{m}^{-2} \text{ s}^{-1})$ from *n*-pentane at 623 K and of hydrogenolysis of ethane $(w_{\text{hydr}}, \text{ mole } \text{m}^{-2} \text{ s}^{-1})$ at 523 K on transition metal blacks

lengthening requires carbone formation activity, furthermore, that rupture of C-C bond is more sensitive for carbon poisoning than that of C-H bond the observed correlation seems to be realistic and emphasizes the importance of carbone formation activity.

The results of O'DONOHOE, CLARKE and ROONEY [7, 8] with W, Nb, Mo, Rh, Pt, Pd films together with our results in references [9, 10] and in this paper permit to suggest that hydrocarbon "build-up" by CH_x insertion is a general phenomenon under conditions of "deep" fragmentation.

Mechanism of isomerization and aromatization on Ni and Co catalysts

First we should like to return and discuss the mechanism of isomer formation observed under hydrogen deficient conditions on various Ni and Co catalysts. From *n*-pentane beside benzene small amount of 2-methylpentane and 2-methylbutane could be observed as well. It is our opinion that 2-methylbutane stems from 2-methylpentane *via* rupturing of the C-C bond between primary and secondary carbon atoms. In 2-methylpentane [14, 15] the reactivity of $C_I - C_{II}$ bond is larger by a factor of 5-8 than that of $C_I - C_{III}$ bond over Ni catalysts. We propose therefore that isomerization of pentane takes place by a CH_x addition — abstraction mechanism. This reaction route, which is completely different from the skeletal rearrangement of hydrocarbons observed on Pt, Ir, Pd catalysts, can be regarded as an "external C_1 shift".

The mechanism of aromatization of 2-methylpentane and 3-methylpentane on Ni and Co catalysts belongs also, according to our opinion, to this



Fig. 10. Toluene/benzene ratio in transformation of 2-methylpentane on 46-Ni-Dep at 603 K (circles) and on 13-Co-Imp at 593 K (squares)

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Fig. 11. Toluene/benzene ratio in transformation of 3-methylpentane on 46-Ni-Dep at 603 K (circles) and on 13-Co-Imp at 593 K (squares)

problem. Theoretically the formation of benzene from methylpentanes requires either bond-shift or C₅-cyclization activity [16]; the *n*-hexane species formed on the surface may then participate in 1,6-ring closure resulting in the formation of benzene. On Pt, Pd catalysts the mechanism of benzene formation can be explained this way. Recent results [17, 18] with ¹³C labelled 3-methylhexane on Pt/Al₂O₃ catalysts have confirmed that beside 1,6-ring closure an additional reaction route is working which involves 1,5-ring closure, ring opening and 1,6-ring closure in the adsorbed phase. As far as Co and Ni catalysts are concerned there is no evidence in the literature for their C₅-cyclization activity. Careful study of transformation of 3-methylpentane over VIIIb Group metals has proved that only Pt, Ir, Rh and Pd promote C₅-cyclization [19]. Skeletal rearrangement activity of Co and Ni could also be ruled out [19].

On the basis of the chain-lengthening activity of Co and Ni catalysts benzene formation from methylpentanes can be interpreted by **carbene insertion** — **methyl abstraction mechanism**. The postulated mechanism consists of the following consecutive steps in the chemisorption phase: carbene insertion into methylpentane resulting in the formation of methylhexane species, 1,6-ring closure followed by the demethylation of toluene. In Figs 10 and 11 the toluene/ benzene ratio formed from 2-methylpentane and 3-methylpentane has been depicted as a function of hydrogen pressure on 46-Ni-Dep and 13-Co-Imp catalyst, respectively. With increasing hydrogen pressure the selectivity of toluene formation decreases since hydrogen promotes demethylation of toluene.

The proposed carbene insertion-methyl abstraction mechanism has been verified by radiotracer experiments, as well. In these experiments ¹⁴C-benzene

Catalyst	T/K	α	<i>Q</i> T / <i>Q</i> B ₀	$\varrho_{\mathbf{B}}/\varrho_{\mathbf{B}^{0}}$
0.9-Ni-B	623	30.5	0.22	0.36
0.9-Ni-B	573	25.5	0.07	0.49
46-Ni-Dep	563	17.8	0.03	0.63
46-Ni-Dep	583	25.6	0.11	0.49
46-Ni-Dep	623	12.1	0.2	0.63

Table VII

Measurements with ¹⁴C-benzene - 2-methylpentane mixtures

 $\alpha-$ conversion in $\%; \varrho_{B^0}-$ initial specific activity of benzene; ϱ_T and ϱ_B are the actual specific activities of toluene and benzene, resp.

has been added to 2-methylpentane/hydrogen mixture. Results are collected in Table VII. According to the carbene insertion model the radioactivity of toluene should be zero if the radioactive benzene is not fragmented. This requirement as shown in Table VII is fulfilled below 615 K. Appearance of inactive toluene confirms the carbene insertion model thus alkylation of benzene could be ruled out. At elevated temperatures fragmentation of benzene may serve as a carbone source, thus the toluene formed becomes radioactive, as well.

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