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ADIUVANTIBUS V. BRUCKNER, GY. DEÁK, K. POLINSZKY, E. PUNGOR, G. SCHAY, Z. G. SZABÓ

> REDIGIT B. LENGYEL

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> redigit B. LENGYEL

> > TOMUS 75

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# PROBLEMS ARISING IN THE ANALYSIS OF THE $H_2O_2-Tl(III)$ SYSTEM

# NEW INDUCED REACTIONS

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# Received November 1, 1971

New induced reactions have been observed during the 1-equivalent oxidation [with cerium(IV) sulfate and/or potassium permanganate] and reduction [by iron(II) ions] of the  $H_2O_2$ -Tl(III) system. The characteristics and the possible mechanisms of induced reactions are given.

Depending on its reaction partners, hydrogen peroxide is capable of 1and 2-equivalent oxidation-reduction reactions. It is also known that the reduction of thallium(III) ions can take place via 2- or 1-equivalent steps. Therefore, we considered it interesting to study the kinetics of the reaction between thallium(III) and hydrogen peroxide. This reaction has long been used in chemical analysis for the reduction of thallium(III), but even so nothing is known as to its mechanism.

For the kinetic investigation planned there was need for an analytical procedure whereby both components of the quenched reaction mixture could be determined simply and rapidly. Exploratory studies have shown that a medium-rate hydrogen peroxide-thallium(III) reaction in a perchloric acid medium can be effectively quenched by the addition of a 20-50-fold excess of sulfate ions and by cooling to 0 °C [1]; we thus concluded that our procedure suggested earlier [2] for the analysis of the  $H_2O_2-H_2S_2O_8$  system might also be used to study the present system. The essence of this procedure is that arsenous acid is added in a known excess to the reaction mixture, and in its presence the hydrogen peroxide is determined cerimetrically. After this titration the excess arsenous acid is also determined cerimetrically in the presence of osmium tetroxide as catalyst. It was thought possible to determine thallium(III) by this latter step because the otherwise slow reaction between arsenous acid and thallium(III) was found to be practically instantaneous in the presence of osmium tetroxide.

Contrary to expectations, however, a large negative deviation was observed in the results for hydrogen peroxide and thallium(III) both in the presence and absence of arsenite. In our view, this deviation is caused by chemical induction and in the present paper we wish to report on these new induced reactions.

# Experimental

The chemicals used in the measurements were stabilizer-free Merck Perhydrol, and other Merck and Fluka p.a. grade products. The solutions were prepared with doubly distilled water. The titrations were carried out by means of a Metrohm Dosimat automatic burette, with efficient stirring, at a rate of 1.0 ml/min. In the impulse titrations use was made of a pulsing relay which actuated the burette at 5 sec intervals, and then caused the addition of 0.01 or 0.05 ml portions of the reagent. The cerimetric determinations were carried out in the presence of ferroin as indicator, while in the permanganate titrations the colour of permanganate was used as indicator. Disregarding those measurements in which the dependence on the initial volume and the acid concentration were studied, the titrations were performed in an initial volume of 60 ml in solutions 0.5 M with respect to sulfuric acid, the titrants being 0.05 N cerium(IV) sulfate or permanganate. After the titration of hydrogen peroxide the residual thallium(III) was reduced with excess arsenous acid; this excess was then determined with cerium(IV) sulfate in the presence of osmium tetroxide as catalyst. In the investigations with iron(II), the absorption of the iron(III) formed was measured with a Unicam SP 500 spectrophotometer at 304 nm in 1 cm silica cells.

#### **Experimental** results

The data in Table I show that in the measurements with cerium(IV) sulfate the change of the concentration ratio  $([Tl(III)]/[H_2O_2])_0$  from 0 to 0.5 results in a linear increase of the H<sub>2</sub>O<sub>2</sub> error, but at higher ratios a limiting

0.	025 M H <sub>2</sub> O <sub>2</sub> ,	ml	$0.025 \ M \ { m Tl}_2({ m SO}_4)_3,  { m ml}$				([TI(III)])	Manner
Taken	Found	Difference	Taken	Found	Difference	Fi	$\left(\frac{1}{[H_2O_2]}\right)_0$	titration
9.89	7.05	-2.84	10.00	7.24	-2.76	0.40	1.011	'a, c
9.89	7.31	-2.58	10.00	7.38	-2.62	0.35	1.011	a, c
9.92	8.87	-1.05	1.02	0.05	-0.97	0.12	0.103	a
9.92	7.83	-2.09	2.05	0.06	-1.98	0.27	0.206	a
9.92	6.80	-3.12	3.07	0.06	-3.01	0.49	0.309	a
9.92	5.78	-4.14	4.10	0.05	-4.14	0.72	0.423	a
9.92	5.55	-4.37	5.12	0.84	-4.28	0.79	0.516	a
9.92	5.63	-4.29	6.10	1.88	-4.22	0.76	0.614	a
9.92	5.44	-4.48	10.24	5.84	-4.40	0.82	1.032	a
9.92	5.23	-4.69	20.48	15.82	-4.66	0.90	2.064	a
4.945	2.92	-2.02	4.00	1.96	-2.04	0.69	0.809	b
9.89	5.71	-4.18	8.00	3.86	-4.14	0.73	0.809	b
9.89	5.63	-4.26	20.00	15.64	-4.36	0.76	2.022	b
9.92	5.46	-4.46	20.48	15.98	-4.50	0.82	2.064	b

Table I

Induced reaction occurring in the  $H_2O_2$ —Tl(III)—Ce(IV) system

a — continuous titration (1 ml/min)

b — impulse titration (0.01 ml/5 sec)

c - in the presence of 1 mM arsenous acid

value is reached. Within the limits of experimental error, the Tl(III) error agrees with that for  $H_2O_2$ . It can be seen from the data that the addition of the titrant solution in impulses of 0.01 ml/5 sec changes the values of the errors only slightly. If the titration error is characterized by an induction factor  $F_i = \Delta[H_2O_2]/[H_2O_2]_{found}$  (equiv./equiv.), then this shows a rapid increase in the presence of smaller amounts of thallium(III), but it does not reach the limiting value of unity.

On the increase of the sulfuric acid concentration the values of the errors decrease slightly, while the dilution of the solution increases the magnitudes of the errors only to an insignificant extent.

It is worth mentioning that if cerium(III) is added (in about a 4-fold excess over hydrogen peroxide), the  $H_2O_2$  error, and with it the Tl(III) error too, increases considerably (Table II).

If titanium(IV) sulfate is added to the solution in about a 4-fold excess over hydrogen peroxide, the value of the  $H_2O_2$  error varies practically linearly up to a ([Tl(III)]/[Tl(I)])<sub>0</sub> ratio of unity and at higher ratios attains a satu-

0.	$025 \ M \ H_2O_2,$	ml	0.02	$0.025 \ M \ { m Tl}_2({ m SO}_4)_3,  { m ml}$			([T](III)])	Manner
Taken	Found	Difference	Taken	Found	Difference	F <sub>i</sub>	$\left(\frac{1}{\left[\mathrm{H}_{2}\mathrm{O}_{2}\right]}\right)_{0}$	of titration
10.00	4.91		10.00	4.88	-5.12	1.04	1.000	a, c
9.92	3.78	-6.14	10.24	4.34	5.90	1.62	1.032	b, c
9.89	3.81	-6.08	15.00	8.78	-6.22	1.60	1.517	b, c
10.00	4.41		20.00	14.24	-5.76	1.27	2.000	b, c
9.92	8.92	-1.00	1.02	0.0	-1.02	0.11	0.103	a, d
9.92	7.84	-2.08	2.05	0.02	-2.02	0.27	0.206	a, d
9.92	6.72	-3.20	3.07	0.07		0.48	0.309	a, d
9.92	5.50	-4.42	4.10	0.17	-4.02	0.80	0.423	a, d
9.92	5.01	-4.91	5.12	0.16	-4.96	0.98	0.516	a, d
9.92	1.38		10.24	1.94		6.19	1.032	a, d
9.92	1.05		15.36	6.80		8.45	1.550	a, d
9.92	4.86		5.12	0.05	-5.07	1.04	0.516	b, d
9.92	0.47	-9.45	10.24	0.44	-9.80	20.11	1.032	b, d
9.92	0.38	-9.54	15.36	6.00	-9.36	25.11	1.550	b, d
9.92	0.38	-9.54	20.48	11.14	-9.34	25.11	2.064	b, d

#### **Table II**

Influence of cerium(III) and titanium(IV) ions on the induced reaction occurring in the  $H_2O_2$ —Tl(III)—Ce(IV) system

a — continuous titration (1 ml/min)

b — impulse titration (0.01 ml/5 sec)

c — in the presence of 1 mM cerium(III) sulfate

d — in the presence of 1 mM titanium(IV) sulfate

	Induced reaction occurring in the $H_2O_2$ — $Tl(III)$ — $KMnO_4$ system									
2.5	$\times 10^{-2} M H_2 0$	$_2$ , ml	2.5×1	$10^{-2} M \operatorname{Tl}_2(\mathrm{SC})$	) <sub>4</sub> ) <sub>3</sub> , ml	F	([TI(III)])	Manne		
Taken	Found	Difference	Taken	Found	Difference	r <sub>i</sub>	$\left(\frac{1}{\left[\mathrm{H}_{2}\mathrm{O}_{2}\right]}\right)_{0}$	titratio		
10.17	9.11	-1.06	1.06	_	_	0.12	0.104	a		
10.17	8.13	-2.02	2.11	-		0.25	0.207	a		
10.17	7.05	-3.12	3.16			0.44	0.312	a		

0.05

0.15

12.22

\_

7.52

0.70

1.05

1.59

7.41

6.95

5.20

5.35

3.20

0.415

0.518

0.622

1.038

2.077

1.494

1.992

1.494

a

a

a

a

a

a. b

a, b

a, c

-4.17

-6.18

-8.90

-7.48

-					111	TT .
	9	h		0		
	<b>ee</b>		л	<b>U</b>		

a — impulse titration (0.05 ml/5 sec)

-4.17

-5.21

-6.25

-8.96

-8.89

-8.42

-8.46

-7.65

4.12

5.27

6.33

10.56

21.12

15.00

20.00

15.00

6.00

4.96

3.92

1.21

1.28

1.62

1.58

2.39

b - in the presence of titanium(IV) sulfate

c — in the presence of cerium(III) sulfate

ration value. In continuous titrations, altogether 10% of the hydrogen peroxide can be determined in the limit, while in impulse titrations this value is only 5%. For both titration methods the induction factor considerably exceeds unity (Table II).

A similar behaviour was observed in the titrations with permanganate (Table III), with the difference that the H<sub>2</sub>O<sub>2</sub> error approaches its limiting value only at lower ([Tl(III)]/[H<sub>2</sub>O<sub>2</sub>])<sub>0</sub> ratios (about 0.7). The value of  $F_i$  in this case is larger than unity. On the application of titanium(IV) sulfate and on the addition of cerium(III) a certain decrease can be observed in the value of  $F_i$ .

**Table IV** 

Spectrophotometric estimation of the total oxidizing capacity of the  $H_2O_2$ —Tl(III) system with iron(II) sulfate reagent

Substances	$E_{\rm calcd.}$	$E_{ m found}$	$\Delta E$
Fe(II) + Tl(III)	-	0.204	_
$ m Fe(II) + H_2O_2$		0.229	-
$\mathrm{Fe(II)} + \mathrm{H_2O_2} + \mathrm{Tl(III)}$	0.433	0.431	-0.002
$\mathrm{Fe(II)}+\mathrm{Tl(III)}+\mathrm{H_2O_2}$	0.433	0.402	-0.031
$[\mathrm{Tl}(\mathrm{III}) + \mathrm{H_2O_2}] + \mathrm{Fe}(\mathrm{III})$	0.433	0.330	-0.103

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10.17

10.17

10.17

10.17

10.17

10.04

10.04

10.04

In the determination of the total oxidizing capacity of the  $Tl(III)-H_2O_2$ system [the absorption of the iron(III) formed was measured at 304 nm after a waiting period of 24 hours], a systematic negative error was observed. This error depends on the order of mixing the reagents: the error is larger when the order of addition of the reagents is iron(II), thallium(III),  $H_2O_2$ , than when it is iron(II),  $H_2O_2$ , thallium(III); this can be seen from Table IV.

# Discussion

It may be concluded from the agreement of the  $H_2O_2$  and Tl(III) errors that these come about as a result of a reaction with the stoichiometry

$$Tl(III) + H_2O_2 = Tl(I) + O_2 + 2 H^+$$
 (1)

However, our measurements show that, in the presence of a 20-fold excess of sulfuric acid over thallium(III), this reaction is so slow ( $t_{8\%} = 960$  min) that even in the case of a titration lasting for 30 min the resulting error scarcely exceeds 1-2%. It must be said, therefore, that the components react in a 1 : 1 molar ratio in some other manner, e.g. via an induced reaction. The occurrence of induced reactions can be expected in every case when different numbers of electrons are involved in the oxidation-reduction couples taking part in the reactions [3]. This holds in the present system, since the oxidation of hydrogen peroxide and the reduction of thallium(III) can both be achieved in 2- or 1-equivalent steps. In advance, however, it is not possible to say whether a coupled or an induced chain reaction will develop.

The primary  $H_2O_2$ -Ce(IV) reaction giving rise to the induced reduction of thallium(III) has been studied in great detail [4-7]. In a sulfuric acid medium the reaction can be characterized by the following mechanism:

$$H_2O_2 + Ce(IV) \rightleftharpoons HO_2 + H^+ + Ce(III)$$
 (2)

$$HO_2 + Ce(IV) \longrightarrow O_2 + H^+ + Ce(III)$$
 (3)

$$HO_2 + Ce(III) \rightleftharpoons Ce(III) \cdot HO_2$$
 (4)

$$Ce(III) \cdot HO_2 + Ce(IV) \longrightarrow O_2 + H^+ + 2 Ce(III)$$
(5)

$$\mathrm{HO}_{2} + \mathrm{HO}_{2} \longrightarrow \mathrm{H}_{2}\mathrm{O}_{2} + \mathrm{O}_{2}$$
 (6)

$$2 \operatorname{Ce(III)} \cdot \operatorname{HO}_2 \longrightarrow \operatorname{H}_2\operatorname{O}_2 + \operatorname{O}_2 + 2 \operatorname{Ce(III)}$$
(7)

$$egin{array}{rcl} k_2 &=& (1.0 \pm 0.1) imes 10^6 \; 1 \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}, \ k_{-2} &=& (1.0 \pm 0.3) imes 10^6 \; 1 \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}, \ k_3 &=& 1.5 imes 10^7 \; 1 \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}, \end{array}$$

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 $egin{array}{rcl} k_4 &=& 60 &\pm 18 \ 1 \cdot {
m mol}^{-1}, \ k_6 &=& (0.9 \pm 0.1) imes 10^6 \ 1 \cdot {
m mol}^{-1} \cdot {
m sec}^{-1}, \ k_7 &=& (4.0 \pm 0.4) imes 10^6 \ 1 \cdot {
m mol}^{-1} \cdot {
m sec}^{-1} \end{array}$ 

Depending on the reaction partner present, the HO<sub>2</sub> radical formed in reaction (2) may be a strong reductant  $(E_{O_2/HO_2}^0 = -0.3 \text{ V})$  or a strong oxidant  $(E_{HO_2/H_2O_2}^0 = 1.7 \text{ V})$  [8]. Being a 2-equivalent reagent, the thallium ion can be classified as a fairly strong oxidant  $(E_{Tl(III)/Tl(I)}^0 = 1.22 \text{ V}$  [9]), while in 1equivalent reactions it can be considered only as a weak oxidant since in this case the strongly oxidizing and weakly reducing thallium(II) intermediate is formed. The formation of thallium(II) has been confirmed optically [10]. The potentials of the Tl(III)-Tl(II) and the Tl(II)-Tl(I) redox couples have not been determined but it is known that thallium(II) can be oxidized to thallium(III) very rapidly by cerium(IV) [11], and further, that reaction (14) leads to equilibrium [14]. Accordingly, the following rough estimate can be given for the oxidation-reduction potentials:

$$E^{0}_{\text{T}(111)/\text{T}(11)} \ge 0.83 \text{ V}, \quad E^{0}_{\text{T}(11)/\text{T}(1)} \le 1.61 \text{ V}$$

Taking into consideration what has been said, the following mechanism can be given for the induced reaction. The  $HO_2$  radical formed in reaction (2) attacks the thallium(III) present:

$$HO_{2} + Tl(III) \longrightarrow O_{2} + H^{+} + Tl(II)$$
 (8)

$$(M \dots HO_2) + Tl(III) \longrightarrow M + O_2 + H^+ + Tl(II)$$
 (8')

The rate coefficient of reaction (8) is not known, but on the basis of the observed behaviour it must be concluded that it cannot be appreciably slower than step (3). The thallium(II) formed in reaction (8) reacts with the hydrogen peroxide present in excess to give  $HO_2$  again:

$$Tl(II) + H_{2}O_{2} \longrightarrow Tl(I) + HO_{2} + H^{+}$$
 (9)

 $k_9 = (2.5 \pm 1) \times 10^7 \ 1 \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ .

With the repetition of chain steps (8) and (9) considerable  $H_2O_2$  and Tl(III) error in a molar ratio of 1:1 can come about. According to our measurements, however, even in the case of that  $([Tl(III)]/[H_2O_2])_0$  ratio which is the most favourable for the induced reaction, the value of  $F_i$  does not reach unity, and thus it must be assumed that  $F_i$  is limited not only by the controlling role of the rates of reactions (3) and (8) but also by the chain termination steps.

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Among these, and especially in the presence of a little hydrogen peroxide, the dismutation of thallium(II) can be assumed:

$$Tl(II) + Tl(II) \longrightarrow Tl(III) + Tl(I)$$
 (10)

 $k_{10} = (2.3 + 0.8) \times 10^6 \, \mathrm{l \cdot mol^{-1} \cdot sec^{-1}},$ 

together with the similarly very fast reaction:

$$Tl(II) + HO_{2} \longrightarrow Tl(I) + O_{2} + H^{+}$$
(11)

 $k_{11} = (2.5 + 1.0) \times 10^{9} \, \mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}.$ 

Step (12) may also lead to shortening of the chain:

$$Ce(IV) + Tl(II) \longrightarrow Ce(III) + Tl(III)$$
 (12)

It was found that the value of  $F_i$  is affected only slightly by the manner of titration, continuous or impulse. This is probably related to the fact that the value of  $k_8$  does not differ significantly from that of  $k_3$ .

Reaction (13) would give rise to  $H_2O_2$  and Tl(III) errors in a ratio different from 1:1

 $2 \operatorname{Ce(IV)} + \operatorname{Tl}(I) = 2 \operatorname{Ce(III)} + \operatorname{Tl}(III)$ (13)

but this is slow under the experimental conditions applied  $(t_{1/2} \approx 2700 \text{ h})$  thus it can be disregarded completely.

The addition of cerium(III) increases the value of  $F_i$ . If cerium(III) merely reverses step (2), then a decrease of  $F_i$  should be observed. However, cerium(III) also forms a complex with the HO<sub>2</sub> radical (reaction (4)) [6], and hence its reactivity is changed considerably. This is evident from the fact that reaction (7) was found to be 4 times faster than reaction (6). It follows directly from this that the relative rate coefficient  $k_3/k_8$  for the case of free HO<sub>2</sub> radicals differs from  $k_5/k_8$ , valid in the presence of a large amount of cerium(III). In practice the latter is found to be smaller than  $k_3/k_8$ .

To explain the extensive increase of the  $H_2O_2$  error in the presence of titanium(IV), we can set out from the observations of CZAPSKI *et al.* [12]. It has been found that the HO<sub>2</sub> radical, the precursor of which in the presence of titanium(IV) is the peroxotitanium(IV) complex, forms an adduct  $[Tl(IV) \ldots H_2O_2 \ldots HO_2]$ . This complex was observed to be about one order of magnitude more stable than the complex formed with cerium(III). Reaction (8') is favoured by the formation of the complex Ce(III)  $\cdot$  HO<sub>2</sub> and, therefore, in the case of the even more stable titanium(IV) complex a further decrease of the relative rate coefficient  $k_5/k_8$ , *i.e.* an even larger induced change,

may be expected. This is found to be so in practice, and under suitable conditions the value of  $F_i$  increases to 25.1 (and the H<sub>2</sub>O<sub>2</sub> error to about 96%).

It should also be mentioned that the determination of the total oxidizing capacity of the  $H_2O_2$ -Tl(III) system is not possible with arsenous acid. Although the rates of the individual reactions of hydrogen peroxide and thallium(III) with arsenous acid become almost instantaneous in the presence of osmium tetroxide as catalyst, at the same time the rate of the reaction between the partners to be determined is increased to an even greater extent. As a result, the value of the total oxidizing capacity is obtained with a negative error. This error can be eliminated by the addition of titanium(IV) sulfate, because owing to the formation of the peroxotitanium(IV) complex, the rate of the catalyzed reaction between the partners remains lower than the rates of the individual reactions with arsenous acid.

Potassium permanganate can act as either a 2- or a 1-equivalent reagent. For this reason, and also on the basis of other observations [2], it can justifiably be assumed that the HQ<sub>2</sub> radical is also formed in this case during the reaction with hydrogen peroxide, and with its help the induced reduction of thallium(III) takes place in the previously reported way. It has been found in connection with induced reactions involving peroxy compounds that, without exception, the extent of the induced change is always greater in the case of permanganate than in that of cerium(IV) sulfate. This regularity also proved to be valid in the present system. In our view, this is related to the fact that the primary reaction with permanganate has a lower rate than in the case of cerium(IV). However, there are no data available in the literature for this assumption to be checked. In addition, little is known as yet about the mechanism of the H<sub>2</sub>O<sub>2</sub>-MnO<sub>4</sub> reaction, and so it appears too early to look for an explanation of the roles of titanium(IV) and cerium(III) in decreasing (perhaps only apparently) the value of  $F_i$ .

Similarly, too few quantitative data are available for the interpretation of the negative error observed when the total oxidizing capacity is determined with iron(II). According to JOHNSON [13], compared to the iron(II)-H<sub>2</sub>O<sub>2</sub> reaction ( $k = 53 \ 1 \cdot mol^{-1} \cdot sec^{-1}$ ) the thallium(III)-iron(II) reaction (k = $= 1.6 \times 10^{-2} 1 \cdot mol^{-1} \cdot sec^{-1}$ ) is reasonably slow and, therefore, it is surprising at first glance that a disturbing induced reaction should take place in the present system. However, if the mechanism of ASHURST and HIGGINSON [14] (which interprets the available experimental data for the latter reaction) is selected as the basis:

$$Tl(III) + Fe(II) \rightleftharpoons Tl(II) + Fe(III)$$
 (14)

$$Tl(II) + Fe(II) \longrightarrow Tl(I) + Fe(III)$$
 (15)

our experimental observations can be readily explained. In the presence of hydrogen peroxide the Tl(II) formed in step (14) can react not only as in

reaction (15) but also as in reaction (9), and in this way the  $HO_{0}$  radical is formed. This latter reacts either by reaction (8) or reaction (16)

$$HO_{a} + Fe(III) \longrightarrow Fe(II) + O_{a} + H^{+}$$
 (16)

 $k_{16} = 1.02 \times 10^5 \,\mathrm{l} \cdot \mathrm{mol}^{-1} \cdot \mathrm{sec}^{-1}$ 

and thus directly or indirectly brings about a decrease of the iron(III) concentration, i.e. it leads to a negative error.

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# VERGLEICH EINIGER AUF ANGABEN THERMISCHER KURVEN BERUHENDER REAKTIONSKINETISCHER BERECHNUNGSMETHODEN

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Aus den Daten von derivatographischen Kurven wurden nach den Methoden von FREEMAN und CARROLL, HOROWITZ und METZGER sowie KISSINGER, unter Anwendung verschiedener Aufheizgeschwindigkeiten, die Aktivierungsenergien und die Reaktionsordnungen der thermischen Zersetzung von Nickel(II)hexamminchlorid, Styrol-Divinylbenzol-Kopolymer und Trichlorfon berechnet. Die nach verschiedenen Methoden bei Reaktionen verschiedener Typen erhaltenen Ergebnisse wurden miteinander verglichen und ausgewertet.

Die Berechnung der reaktionskinetischen Daten der bei kontinuierlicher Aufheizung ablaufenden Zersetzungsvorgänge beschäftigt die Forscher in letzterer Zeit in zunehmendem Maße, da eine solche Berechnung fallweise wesentlich weniger Versuche und Zeit erfordert, als die Berechnung aus Isothermen.

Auf thermoanalytischen Kurven beruhende Berechnungsmethoden sind von mehreren Autoren entwickelt worden. Bei ihren Ableitungen gehen sie aus der Geschwindigkeitsgleichung und aus der die Temperaturabhängigkeit der Geschwindigkeitskonstante angebenden Arrheniusschen Gleichung aus. Nach verschiedenen mathematischen Operationen gelangen sie zu dem in den kinetischen Berechnungen verwendeten Endzusammenhang. In den mathematischen Operationen werden jene Glieder (z. B. Frequenzfaktor, Konzentration) aus der Geschwindigkeitsgleichung bzw. aus der Arrheniusschen Gleichung eliminiert, deren Bestimmung aus den thermischen Kurven mit Schwierigkeiten verbunden ist. Die richtige Wahl dieser Glieder bestimmt die Brauchbarkeit der Methode.

In der vorliegenden Arbeit wurden die kinetischen Parameter von drei Reaktionen verschiedenen Typs mit Hilfe von drei, von verschiedenen Verfassern entwickelten unterschiedlichen Zusammenhängen berechnet. Die nötigen Daten wurden derivatographischen Kurven entnommen. Die thermische Zersetzung wurde in sämtlichen Versuchen in einer Stickstoffatmosphäre durchgeführt.

#### FLÓRA: REAKTIONSKINETISCHE BERECHNUNGSMETHODEN

# Mechanismus der untersuchten thermischen Reaktionen

Der thermische Zerfall von Nickel(II)hexamminchlorid wurde untersucht. Diese Verbindung wird in einem verhältnismäßig deutlich abgesonderten Vorgang, unter Abspaltung von vier Molekülen gasförmigen Ammoniak, zu festem Nickel(II)diamminchlorid zersetzt, wie in der aufgeschriebenen Reaktionsgleichung angegeben ist [1]:

$$[Ni(NH_3)_6]Cl_{2(fest)} \rightarrow [Ni(NH_3)_2]Cl_{2(fest)} + 4NH_{3(Gas)}$$

In Abhängigkeit von der Aufheizgeschwindigkeit verläuft die Zersetzung bei 150–200 °C mit der höchsten Geschwindigkeit.

Die nächste untersuchte Verbindung war das Styrol-Divinylbenzol-Kopolymer, dessen Zersetzungsmechanismus nicht genau bekannt ist. Aus den bei verschiedenen Temperaturen erhaltenen Erhitzungsrückständen konnte jedenfalls mit IR-spektrometrischen Untersuchungen festgestellt werden, daß ausschließlich gasförmige Zersetzungsprodukte entstehen; das Spektrum der bei verschiedenen Zersetzungstemperaturen erhaltenen Rückstände war nämlich in sämtlichen Fällen mit dem IR-Spektrum des Ausgangsmaterials identisch [2]. Die Reaktion kann formell wie folgt aufgeschrieben werden:

Styrol-Divinylbenzol-Kopolymer<sub>(fest)</sub>  $\rightarrow$  Gas + Gas

Je nach der Aufheizgeschwindigkeit ist die Zersetzungsgeschwindigkeit bei 360-440 °C maximal [3].

Die dritte untersuchte Verbindung, das unter dem Namen Dipterex oder Trichlorfon bekannte Pflanzenschutzmittel, schmilzt beim Erwärmen und zersetzt sich dann gemäß folgender Reaktionsgleichung:



wobei gasförmige Salzsäure abgespalten wird und flüssiges DDVP entsteht. Die thermische Dissoziation des DDVP beginnt sozusagen parallel mit seiner Entstehung; die beiden Zersetzungsvorgänge überdecken sich gewissermaßen. Der Zerfall von Dipterex verläuft — in Abhängigkeit von der Aufheizgeschwindigkeit — bei 166—216 °C mit der Höchstgeschwindigkeit [4].

#### FLÓRA: REAKTIONSKINETISCHE BERECHNUNGSMETHODEN

# In den kinetischen Berechnungen verwendete Zusammenhänge

Die Zersetzungskinetik der genannten drei Reaktionen verschiedenen Typs wurde nach den Methoden von FREEMAN und CARROLL [5], HOROWITZ und METZGER [7] sowie von KISSINGER [8] berechnet.

Nach FREEMAN und CARROLL [5] kann die Aktivierungsenergie  $E^*$  aus der Richtungstangente ( $-E^*/R$ ) der durch Darstellung der zusammengehörenden X und Y-Werte der Gl. (1)

$$\frac{\Delta \ln h_i}{\Delta \ln (W - w_i)} = -\frac{E^*}{R} \cdot \frac{\Delta \frac{1}{T_i}}{\Delta \ln (W - w_i)} + n \tag{1}$$

erhaltenen Geraden berechnet werden. Der Schnittpunkt der Geraden mit der Y-Achse gibt die Ordnung n der Reaktion an. In Gl. (1) bedeutet  $h_i$  den zu verschiedenen Temperaturen  $T_i$  zugeordneten DTG-Galvanometerausschlag in mm,  $w_i$  den Gewichtsverlust bei verschiedenen Temperaturen  $T_i$ , W den gesamten Gewichtsverlust, R die universelle Gaskonstante.

Der genannte Zusammenhang ist eigentlich eine bereits modifizierte Form des ursprünglichen Zusammenhangs von FREEMAN und CARROLL [6]. Diese Verfasser bestimmen die Geschwindigkeit der Gewichtsveränderung  $dw_i/dt$  von Punkt zu Punkt aus der TG-Kurve. Der Abstand der einzelnen Punkte der derivatographischen DTG-Kurve von der Grundlinie h ist der Geschwindigkeit der Gewichtsveränderung proportional. Da in der Gleichung von FREEMAN und CARROLL mit der Differenz von Logarithmen gerechnet wird, kann man an Stelle des Absolutwertes der Geschwindigkeit der Gewichtsveränderung mit dem diesem proportionalen DTG-Galvanometerausschlag harbeiten; letzterer Wert (in mm) ist vom Derivatogramm leicht ablesbar.

Nach der Methode von HOROWITZ und METZGER [7] wird die Aktivierungsenergie aus der Richtungstangente der durch Darstellung der X- und Y-Werte gemäß Gl. (2)

$$\ln \ln \frac{W}{W - w_i} = \frac{E^*}{RT_s^2} \cdot \Theta \tag{2}$$

erhaltenen Geraden berechnet. In Gl. (2) ist  $W/(W - w_i)$  die Konzentration des noch unzersetzten Materials bei der Temperatur  $T_i$ ,  $T_s$  die Spitzentemperatur und  $\Theta = T_i - T_s$ .

Dieser Zusammenhang kann nur dann angewendet werden, wenn die Reaktion erster Ordnung ist, oder wenn bei der Zersetzung ausschließlich gasförmige Produkte entstehen, die sofort aus dem System entweichen.

Ist die Reaktion nicht erster Ordnung, bzw. entstehen bei der Zersetzung flüssige oder feste Intermediärprodukte, so kann die Aktivierungsenergie nach Horowitz und METZGER aus folgendem Zusammenhang berechnet werden:

$$\ln \frac{1 - \left(\frac{W - w_i}{W}\right)^{1 - n}}{1 - n} = \frac{E^*}{RT_s^2} \cdot \Theta$$
(3)

Zur Berechnung ist — außer den bereits genannten Daten — die Kenntnis der Reaktionsordnung *n* notwendig. Der Wert von *n* wird aus dem Zusammenhang zwischen dem zum Inflexionspunkt der TG-Kurve gehörenden Konzentrationswert und der Reaktionsordnung bestimmt.

In Kenntnis der Spitzentemperaturen  $T_s$ , die aus mit verschiedenen Aufheizgeschwindigkeiten  $\Phi$  aufgenommenen Derivatogrammen ablesbar sind, kann die Aktivierungsenergie nach der Methode von KISSINGER [8] aus je zwei zusammengehörenden Werten oder aus der Richtungstangente der durch Darstellung der zusammengehörenden X- und Y-Werte der Gleichung

$$d\left(\ln\frac{\Phi_2}{T_s}\right) = -\frac{E^*}{R} \cdot d\frac{1}{T_s}$$
(4)

erhaltenen Kurve berechnet werden. KISSINGER bestimmt die Reaktionsordnung aus dem Zusammenhang  $n = 1.26 \sqrt{s}$ , wo s der Shape-Index ist, dessen Berechnungsmethode der Verfasser ausführlich angibt.\*

# Ergebnisse der Berechnungen

# Aktivierungsenergien der Zersetzungsreaktionen

Die aus mit verschiedenen Aufheizgeschwindigkeiten aufgenommenen Derivatogrammen, mit verschiedenen Methoden berechneten Aktivierungsenergiewerte sind in Tab. I zusammengestellt.

Die Aktivierungsenergie der Zersetzung des Nickel(II)hexamminchlorids nimmt — nach der Methode von FREEMAN und CARROLL berechnet mit steigender Aufheizgeschwindigkeit anfänglich ab und nähert sich dann einem Grenzwert um etwa 14 kcal/Mol. MURGULESCU und SEGAL [9] fanden in unter isothermen Bedingungen ausgeführten Messungen für diese Verbindung einen Wert von 14,34 kcal/Mol; die Übereinstimmung mit unseren Ergebnissen ist also verhältnismäßig gut.

\* In der vorliegenden Arbeit wurde, von den Originalbezeichnungen in den Geschwindigkeitsgleichungen der verschiedenen Verfasser abweichend, eine Bezeichnungsart angewendet, in der Größen identischer Bedeutung mit identischen Buchstaben bezeichnet werden. So bezeichnen z. B. HOROWITZ und METZGER die Größe W mit  $W_0$  für den Fall, wenn ausschließlich gasförmige Zersetzungsprodukte entstehen bzw. mit  $(W_0 - W_i)$ , wenn auch flüssige und feste Produkte gebildet werden.  $(W - w_i)$  wird bei FREEMAN und CARROLL mit  $W_c - W = W_r$ , bei HOROWITZ und METZGER mit  $(W - W_i^{\ell})$  bezeichnet.

#### FLÓRA: REAKTIONSKINETISCHE BERECHNUNGSMETHODEN

T	al	e	lle	T

		<i>E</i> *					
Verbindung	Aufheiz- geschwindigkeit °C/Minute	KISSINGER	Horowitz – Metzger 1	HOROWITZ – METZGER 2	Freeman- Carroll	Literatur	
[Ni(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>2</sub>	0,7			20,7	21,3		
	4,1		1	17,0	18,3		
	5,1	$(44,6)^{a}$		16,7	14,4	14,34	
	6,9			14,5	16,3		
	9,2			15,3	14,2		
Styrol-Divinylbenzol-							
Kopolymer	0,9		29,6		28,3		
		29,0					
	2,6		34,6		33,8		
	5,3	$(24,0)^{a}$	36,3		34,2		
	8,6		36,3		36,2		
		20,8		· . ·			
	10,3		37,4	Er .	36,1		
Trichlorfon	1,6		29,9	1	33,7		
		6,4					
	2,2		28,2		23,5	24,8	
		18,1				$\pm 0,5$	
	7,4		33,0		23,0		
	11,1	$(17,8)^{a}$	38,8	1	23,2		

Nach verschiedenen Methoden berechnete Aktivierungsenergiewerte

<sup>a</sup> Aus der Kurve berechnet

Die nach der Berechnungsmethode von HOROWITZ und METZGER erzielten Werte zeigen eine gute Parallelität zu den mit der FREEMAN-CARROLL-Methode erhaltenen Aktivierungsenergien. Zwischen den mit diesen beiden Methoden erhaltenen Aktivierungsenergien ergab sich ein Unterschied von höchstens 2,3 kcal/Mol.

Bei Anwendung der Methode von KISSINGER erhielten wir bei der Berechnung aus je zwei experimentellen Punkten in einigen Fällen Ergebnisse, die in der Nähe des Literaturwerts lagen. Bei der Berechnung aus der Richtungstangente der aus mehreren Punkten aufgezeichneten Kurve ergab sich ein Wert von 44,60 kcal/Mol, also von den übrigen Ergebnissen wesentlich abweichend.

Die nach den Methoden von FREEMAN und CARROLL bzw. HOROWITZ und METZGER berechneten Werte für die Aktivierungsenergie der thermischen Zersetzung von Styrol-Divinylbenzol-Kopolymer zeigen eine gute Überein-

stimmung. Im Gegensatz zu der vorangegangenen Verbindung zeigte sich hier eine Zunahme der Aktivierungsenergie mit der Aufheizgeschwindigkeit, und zwar eine Änderung von 28,3 kcal/Mol bis 37,40 kcal/Mol.\* Mit der Methode von KISSINGER wurden in der Mehrzahl der Fälle wesentlich kleinere Werte erhalten als mit den beiden anderen Methoden.

Für die Aktivierungsenergie der Zersetzung des Trichlorfons wurde bei Anwendung der Methode von FREEMAN und CARROLL — abgesehen vom Wert von 33,7 kcal/Mol bei der Aufheizgeschwindigkeit von 1,6 °C/Minute — ein Wert um 23 kcal/Mol gefunden. Dieser ist in verhältnismäßig guter Übereinstimmung mit dem Wert von 24,8  $\pm$  0,5 kcal/Mol, der durch sowjetische Verfasser [12] in wäßriger Lösung, unter Anwendung einer polarographischen Methode gemessen wurde. Die Ergebnisse bei der Anwendung der Methoden von HOROWITZ und METZGER bzw. von KISSINGER wichen in meisten Fällen wesentlich von den nach FREEMAN und CARROLL erhaltenen Werten ab.

# Ordnung der Zersetzungsreaktionen

Aus der Bestimmung der Reaktionsordnung nach verschiedenen Verfahren wurde festgestellt, daß die Reaktionsordnung von der Aufheizgeschwindigkeit abhängig ist (Tab. II). Die Ordnung der Zersetzungsreaktion beträgt bei Nickel(II)hexamminchlorid 0-0,6, bei dem Styrol-Divinylbenzol-Kopolymeren 0,5-1, bei Trichlorfon ungefähr 1.

# **Diskussion der Ergebnisse**

# Aktivierungsenergie

Die nach der Methode von KISSINGER erhaltenen Ergebnisse weichen — wie ersichtlich — bei allen drei untersuchten Reaktionen in der Mehrzahl der Fälle von den nach anderen Methoden erhaltenen Ergebnissen ab.

Bekanntlich kann der Temperaturmeßfehler der Derivatographie bei gegebener Empfindlichkeit (im Fall von Trichlorfon 300 °C) sogar  $\pm 6$  °C betragen. Da die Methode von KISSINGER die genaue Kenntnis des Absolut-

<sup>\*</sup> Es soll hier erwähnt werden, daß die thermischen Eigenschaften dieses Kopolymeren auch vor vier Jahren untersucht worden sind. Damals fanden wir eine höhere thermische Stabilität und eine höhere Aktivierungsenergie der Zersetzung. Bei einer Aufheizgeschwindigkeit von ungefähr 5 °C/Minute erhielten wir einen Wert von 48 kcal/Mol, in ziemlich guter Übereinstimmung mit den Werten von FREEMAN und CARROLL [5] sowie JELLINEK [10], nämlich 46 bzw. 44 kcal/Mol. Die Abnahme der thermischen Stabilität und der Aktivierungsenergie der Zersetzung wurde durch die Alterung des Kopolymeren im Laufe der vergangenen vier Jahre verursacht. Über die Untersuchung der Alterung von Polymeren mit Hilfe derivatographischer Methoden haben wir in unserer Mitteilung über die Untersuchung der thermischen Eigenschaften des Polypropylens berichtet [11].

# **Tabelle II**

		n			
Verbindung	Aufheiz- geschwindigkeit °C/Minute	Kissinger	Horowitz – Metzger	Freeman — Carroll	
[Ni(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>2</sub>	0,7	0,25	0,25	1	
	4,1	0,34	0,32	0,1	
	5,1	0,37	0,36	-0,6	
	6,9	0,60	0,50	0,2	
	9,2	0,61	0,54	0,2	
Styrol-Divinylbenzol-					
Kopolymer	0,9	0,58	0,47	0	
	2,6	0,64	0,70	0	
	5,3	0,75	0,74	0	
	8,6	0,98	0,95	0	
	10,3	0,97	0,88	0	
Trichlorfon	1,6	1,07	0,87	1	
	2,2	0,93	0,78	1	
	7,4	1,14	1,00	1	
	11,1	1,00	0,80	1	

### Nach verschiedenen Methoden berechnete Reaktionsordnungen

werts der Spitzentemperatur erfordert, fällt ein Meßfehler bei ihrer Bestimmung im Endergebnis schwer ins Gewicht. Zugleich muß auch die Aufheizgeschwindigkeit genau bekannt sein. Um diese Einflüsse zu klären, wurden Berechnungen durchgeführt, welche Änderungen im Wert der Aktivierungsenergie durch einen Fehler von 5 °C bei der Temperaturbestimmung bzw. durch einen Fehler von 0,3 °C/Minute bei der Bestimmung der Aufheizgeschwindigkeit bedingt werden.

Unsere Berechnungen zeigten, daß Fehler von  $\pm 5$  °C bzw.  $\pm 0.3$  °C/ Minute einen Fehler von 10—20 kcal/Mol im Wert der Aktivierungsenergie verursachen können. Je höher die Temperatur ist, bei der der Meßfehler von 5 °C begangen wird, desto größer ist der Fehler bei der Berechnung der Aktivierungsenergie.

Wie erwähnt wurde, stimmen die Aktivierungsenergiewerte nach FREEMAN und CARROLL bzw. nach HOROWITZ und METZGER bei der Zersetzung von Nickel(II)hexamminchlorid und Styrol-Divinylbenzol-Kopolymer ziemlich gut überein bzw. sie weisen nur geringe Abweichungen voneinander auf, während bei der Zersetzung von Trichlorfon auch diese Methoden stark abweichende Werte ergeben. Bei der Methode von HOROWITZ und METZGER müssen die Spitzentemperaturen, die zu den verschiedenen Temperaturen  $T_i$  gehörenden Konzentrationswerte und bei bestimmten Reaktionstypen der Absolutwert der Reaktionsordnung genau bekannt sein.

Für den Wert der Reaktionsordnung bei der Zersetzung von Trichlorfon ergab sich, nach verschiedenen Methoden berechnet, stets etwa 1. Wurde die Reaktionsordnung nicht ganz genau bestimmt, d.h. ihr Wert könnte 0,8 oder auch 1,2 betragen, so erfüllt die durch Darstellung der experimentell bestimmten X- und Y-Werte erhaltene Kurve die in Gl. (3) enthaltene Bedingung nicht, d.h. sie geht nicht durch den Koordinatenausgangspunkt (Abb. 1). Durch



Abb. 1. Nach HOROWITZ und METZGER berechnete kinetische Kurven der Zersetzung von Trichlorfon bei verschiedenen Werten von n und  $T_s$ 

Einsetzen verschiedener Werte von n kann jene Reaktionsordnung gefunden werden, bei der die experimentell bestimmte Kurve — bei der gemessenen Spitzentemperatur — den Forderungen entspricht. Auf diese Weise könnte der richtige Wert der Reaktionsordnung, falls die Spitzentemperatur richtig gewählt wurde, angenähert werden. Im geprüften Fall ergibt sich für n der Wert 0,9.

Wurde die Spitzentemperatur ungenau bestimmt und ihr richtiger Wert beträgt z. B. 186,5 °C, so verschiebt sich die Kurvenschar und eine andere Kurve, die einem geringeren *n*-Wert als 0,9 entspricht, wird durch den Koordinatenausgangspunkt gehen.

Unsere Berechnungen aufgrund der Kurvenschar zeigten, daß — falls die Spitzentemperatur genau gemessen wurde — ein Irrtum von 0,1 im Wert der Reaktionsordnung eine Abweichung von 1 kcal/Mol in der Aktivierungsenergie hervorruft. Wurde die Reaktionsordnung genau bestimmt, so erfolgt aus einem Irrtum von 5 °C in der Spitzentemperatur ebenfalls ein Fehler von ungefähr 1 kcal/Mol im Wert der Aktivierungsenergie. Wie ersichtlich, verursachen also Fehler in der Bestimmung der Reaktionsordnung und der Spitzentemperatur keine wesentlichen Fehler in der Berechnung der Aktivierungsenergie nach der Methode von HOROWITZ und METZGER.

#### FLÓRA: REAKTIONSKINETISCHE BERECHNUNGSMETHODEN

Dagegen sind bei diesem Berechnungsverfahren Ungenauigkeiten in der Bestimmung der zu den einzelnen Temperaturen  $T_i$  gehörenden Konzentrationswerten von größerer Bedeutung hinsichtlich des Fehlers des Endergebnisses.

Bei der Besprechung des Zersetzungsmechanismus von Trichlorfon wurde bemerkt, daß der thermische Dissoziationsprozeß der Verbindung selbst und ihrer Zersetzungsprodukte einander überdecken. Demzufolge ist es unmöglich, die Konzentration des noch unzersetzten Trichlorfons bei einer bestimmten Temperatur richtig anzugeben.



Abb. 2. Nach HOROWITZ und METZGER berechnete kinetische Kurven der Zersetzung von Trichlorfon bei verschiedenen Werten von W und  $w_i$ 

Der richtige Wert dieser Konzentration könnte auf folgende Art angenähert werden: Bei einer Einwaage von 100 mg erzeugt die Abspaltung von einem Salzsäuremolekül eine Gewichtsabnahme von W = 14.2 mg. Die Menge der in der ersten Zersetzungsstufe entweichenden flüchtigen Zersetzungsprodukte ist jedoch - infolge der Überlappung der Zersetzungsvorgänge — wesentlich höher. Wird in der Gleichung nach HOROWITZ und METZGER (Gl. 2) mit einer Gesamtmenge von W = 61,6 mg an flüchtigen Stoffen gerechnet, so gelangt man bei der Darstellung der X- und Y-Werte zu Kurve 1 in Abb. 2. Wird der Wert von W zu 14,2 mg gewählt und die Berechnung nur bis zu jener Temperatur (etwa 200 °C) geführt, bei der die Probe diesen Gewichtsverlust erreicht, so gelangt man zu Kurve 2 in Abb. 2. Keiner dieser Fälle ist richtig, da die Zersetzung von Trichlorfon bis zu DDVP nicht 61,6 mg, sondern 14,2 mg flüchtige Stoffe ergibt, wobei dieser Vorgang nicht bis 200 °C, sondern bis 240 °C dauert. Die richtige kinetische Kurve der Trichlorfon-Zersetzung könnte Kurve 3 in Abb. 2 sein, die unter Verwendung zweier Punkte gezeichnet wurde. Der eine ist Punkt 1 von Kurve 2, da angenommen werden kann, daß der Gewichtsverlust am Anfang des Vorganges ausschließlich aus der Zersetzung des Trichlorfons stammt. Bei der Berechnung des anderen Punktes gingen wir von der Annahme aus, daß bei 233 °C zum völligen Zerfall von Trichlorfon bis zu DDVP noch 2,4 mg ( $W-w_i = 2,4$  mg) Salzsäure abgespaltet werden müssen. Aus der Richtungstangente der auf diese Weise erhaltenen Geraden ergibt sich für die Aktivierungsenergie ein Wert von 28,6 kcal/Mol; dieser stellt bereits eine bessere Annäherung des richtigen Wertes dar, als der aus Kurve 1 erhaltene Wert von 38,8 kcal/Mol, bzw. der aus Kurve 2 erhaltene

Wert von 43,6 kcal/Mol. (Die Berechnungen wurden mit den Punkten der bei einer Aufheizgeschwindigkeit von 11,1 °C/Minute aufgenommenen Kurve durchgeführt.)

Bei der Berechnung der in Tab. I angeführten Ergebnisse wurde für W die Gesamtmenge des in der ersten Zersetzungsstufe entweichenden flüchtigen Anteils, d. h. 61,60 mg eingesetzt. Daraus ergab sich der von dem in der Literatur angegebenen Wert wesentlich abweichende berechnete Wert nach HOROWITZ und METZGER.

Bei der Zersetzung des Nickel(II)hexamminchlorids und des Styrol-Divinylbenzol-Kopolymers spielen sich keine überlappenden Vorgänge ab, folglich kann die Konzentration des noch unzersetzten Stoffes bei verschiedenen Temperaturen bzw. in verschiedenen Zeitpunkten genau bestimmt werden. Daraus ergibt sich die gute Übereinstimmung der nach FREEMAN und CARROLL bzw. nach Horowitz und Metzger berechneten Ergebnisse.

Merkwürdigerweise wurde nach der Methode von FREEMAN und CARROLL bei höheren Aufheizgeschwindigkeiten auch im Falle der Trichlorfon-Zersetzung eine mit den Literaturangaben [12] übereinstimmende Aktivierungsenergie gefunden, obwohl die überlappenden Vorgänge auch in der Bestimmung bei dieser Methode benötigten Daten ( $w_i$  und  $h_i$ ) zu Fehlern führen.

Unter den experimentell bestimmten Daten entsprechen die  $T_i$ -Werte annähernd den richtigen Werten, da die Zersetzung von Trichlorfon im bezeichneten Temperaturbereich verläuft. Da mit der Differenz von Logarithmen gerechnet wird, beeinflußt der beim Ablesen der Gewichtsverminderung  $w_i$ , bzw. der mit der Geschwindigkeit der Gewichtsveränderung proportionalen  $h_i$ -Werte begangene Fehler den Wert der Aktivierungsenergie in dem Fall nicht, wenn die aus der Zersetzung des DDVP stammenden Gewichtsveränderung bzw. deren Geschwindigkeit, die aus der Zersetzung des Trichlorfons stammenden Gewichtsveränderung bzw. deren Geschwindigkeit bei jeder einzelnen Temperatur  $T_i$  proportional erhöht. (Es kann angen nommen werden, daß dies tatsächlich der Fall ist.)

Bei der Berechnung der Aktivierungsenergie der zweiten Zersetzungsstufe, d. h. der Zersetzung des DDVP meldet sich der infolge der Überlappung der Zersetzungsvorgänge entstehende Fehler der Bestimmung der experimentellen Punkte viel deutlicher.

Die Aktivierungsener gie der reinen DDVP-Zersetzung ergab sich nach FREEMAN und CARROLL — je nach der Aufheizgeschwindigkeit — zu 6—10 kcal/Mol. Wurde die Aktivierungsenergie aus der zweiten Stufe des Trichlorfon-Derivatogramms berechnet, so erhielten wir bei höheren Aufheizgeschwindigkeiten  $(5-10 \, ^{\circ}C/Minute) 22-31,5 \, kcal/Mol.$  Im letzteren Fall wurden die in der Berechnung verwendeten Ausgangsdaten  $T_0$ ,  $h_0$  und  $s_0$  bei dem Knickpunkt der DTG-Kurve (die die Trennung der beiden Zersetzungsvorgänge anzeigt) abgelesen. Wegen der Überlappung der Vorgänge kehrt die DTG-Kurve nach Beendigung der Trichlorfon-Zersetzung nicht zur Grundlinie zurück, sondern der Knickpunkt befindet sich in einem bestimmten Abstand  $h_0$  von der Grundlinie (Abb. 3). Der  $h_0$ -Wert ist höher als der der Zersetzungsgeschwindigkeit des reinen DDVP bei der abgelesenen Temperatur  $T_0$  entsprechende Wert. Wird mit einem  $h_0$ -Wert gerechnet, der höher als der richtige Wert ist, so erhält man nach unseren Berechnungen für die Aktivierungsenergie einen niedrigeren als ihr richtiger Wert.

wird mit einem  $n_0$ -wert gerechnet, der hoher als der hentige wert ist, so einatt man hach unseren Berechnungen für die Aktivierungsenergie einen niedrigeren als ihr richtiger Wert. Auch der in der Berechnung verwendete  $T_0$ -Wert liegt höher als die Anfangstemperatur der DDVP-Zersetzung, da diese Zersetzung bereits bei einer wesentlich unterhalb des Knickpunktes der DTG-Kurve liegenden Temperatur  $T_k$  beginnt. Wird mit einem oberhalb des richtigen Wertes liegenden  $T_0$ -Wert gerechnet, so erhält man für die Aktivierungsenergie einen höheren Wert als ihr richtiger Wert. Die beim Ablesen von  $h_0$  und  $T_0$  begangenen Fehler können einander im Glücksfall ausgleichen; praktisch dominiert jedoch — je nach dem Maß der Überlappung der Vorgänge — einmal dieser, das andere Mal jener Fehler. Auch der Fehler der Bestimmung von  $w_i$  beeinflußt den berechneten Wert der Aktivierungsenergie wesentlich.

#### FLÓRA: REAKTIONSKINETISCHE BERECHNUNGSMETHODEN



Abb. 3. Derivatogramm von Trichlorfon

# Reaktionsordnung

Die nach den Methoden von HOROWITZ und METZGER bzw. von KISSINGER erhaltenen Werte der Reaktionsordnung sind verläßlicher als die nach FREE-MAN und CARROLL erhaltenen, weil im letzteren Fall eine geringfügige Verschiebung der Richtungstangente der kinetischen Kurve (eine solche Verschiebung ergibt sich aus der Streuung der Versuchspunkte) bereits zu einer wesentlichen Änderung im Wert des Achsenabschnitts führt.

# Schlußfolgerungen

Durch Vergleich der verschiedenen Methoden zur Berechnung der Aktivierungsenergie der Zersetzung könnte festgestellt werden, daß die Methoden von FREEMAN und CARROLL sowie von HOROWITZ und METZGER in Fällen, wo die thermischen Vorgänge gut gesondert sind, gleichermaßen gut anwendbar sind. Überlappen sich die thermischen Vorgänge, so dürfen die erhaltenen Werte der Aktivierungsenergie nur mit Vorbehalt akzeptiert werden. Die Anwendung der verhältnismäßig einfach zu handhabenden Methode von KISSINGER wird durch den Umstand beschränkt, daß eine genauere Kenntnis der Spitzentemperaturen notwendig ist als die Genauigkeit der derivatographischen Temperaturmessung.

Hinsichtlich der Wahl der zur Berechnung benötigten Daten ist es ein Vorteil der Methode von FREEMAN und CARROLL gegenüber den beiden anderen Methoden, daß diese Verfasser mit der Differenz von Logarithmen arbeiten, wodurch keine Absolutwerte der Daten (Konzentration, Spitzentemperatur, Geschwindigkeit des Gewichtsverlustes), sondern nur die Kenntnis proportionaler Größen (Gewichtsverlust, Temperatur, Galvanometerausschlag) benötigt werden. Ein weiterer Vorteil dieser Methode besteht darin, daß aus einer einzigen Aufnahme gearbeitet wird. Auch Horowitz und METZGER arbeiten aus einer Aufnahme, jedoch ist die Kenntnis des Absolutwertes der Spitzentemperatur, der Konzentration und der Reaktionsordnung erforderlich. Die Anwendung der Methode von KISSINGER benötigt mehrere, bei verschiedenen Aufheiztemperaturen aufgenommene Kurven. In seiner Gleichung rechnet KISSINGER zwar mit der Differenz von Logarithmen, jedoch meldet sich der bei der Bestimmung der Absolutwerte der Spitzentemperaturen begangene Fehler trotzdem, da dieser Fehler nicht in sämtlichen Fällen gleich ist.

Die Berechnungen wurden mit einem Computer durchgeführt, für den wir ein entsprechendes Programm ausgearbeitet haben. Die Laufzeit des Programms beträgt 3-5 Minuten.

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# ETHYLENEDIAMINE COMPLEXES OF NICKEL(II)

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A study was made of the visible and infrared spectra and the magnetic properties of  $[Ni(en)_3]X_n$   $(n = 1, 2; X = Cl^-, Br^-, I^-, S_2O_3^-, PtCl_4^{--})$  and  $[Ni(en)_2]Y_n$   $(n = 1, 2; Y = Cl^-, Br^-, AgI_2^-, CuI_2^-, HgI_4^{--}, Ag(CN)_2^-, Zn(CN)_4^{--}, Cd(CN)_4^{--})$ . Some of the experimental results are interpreted on the basis of the ligand-field theory. The probability of detecting the bands relating to the  $\nu(NiN)$  vibrations is discussed in detail; for the above compounds these bands are to be found at 500-540 cm^{-1}.

# Introduction

Of the ethylenediamine (en) complexes of nickel(II) the tris complex has been studied in the greatest detail. Since the ligand is bidentate, the complex ion Ni $(en)_3^{2+}$  belongs to the  $D_3$  symmetry group, but its spectral, magnetic and other properties can also be well treated on the basis of the octahedral model.

Under suitable conditions square planar nickel(II)-en complexes exist too. If  $[Ni(en)_2(H_2O)_2]^{2+}$  is heated in alcohol, square planar  $[Ni(en)_2]^{2+}$  is formed; this is proved by the structure of the absorption spectrum [1]. The square planar form can be stabilized and isolated by reaction with complex anions in the case of suitable stoichiometric ratios of the components [2]. With the use of AgBrI<sup>-</sup>, AgI<sup>-</sup><sub>2</sub>, CuI<sup>-</sup><sub>2</sub>, HgI<sup>2-</sup><sub>4</sub> or Ag(CN)<sup>-</sup><sub>2</sub>, for instance, compounds of the type  $[Ni(en)_2]X_n$  can be isolated; these are stable only in the solid state, however, and in solution they dissociate and undergo transformation.

In the present paper the visible and infrared spectra and the magnetic properties are reported for compounds of the type  $[Ni(en)_3]X_n$   $(n = 1, 2; X = Cl^-, Br^-, I^- \{type a\}, S_2O_3^{2^-}, PtCl_4^{2^-})$  and  $[Ni(en)_2]Y_n$   $(n = 1, 2; Y = Cl^-, Br^- \{type b\}, AgI_2^-, CuI_2^-, HgI_4^{2^-} \{type c\}, Ag(CN)_2^-, Zn(CN)_4^{2^-}, Cd(CN)_4^{2^-} \{type d\})$ , and the results are interpreted on the basis of the ligand-field theory.

# Experimental

The complexes were prepared by methods already reported in the literature [2, 3], or by methods analogous to these. Their compositions were checked by analysis of C, H and Ni.

The visible and near-infrared spectra were obtained with a Beckman DU spectrophotometer. For the tris complexes the solvent contained 5% en; in the case of the complexes  $[Ni(en)_2]Cl_2$  and  $[Ni(en)_2]Br_2$  measurements were carried out both with and without an en excess.

A MgO standard was applied in the course of determining the reflection spectra, and the KUBELKA-MUNK relation [4] was used in the calculations.

The infrared spectra were measured in the range 375-8750 cm<sup>-1</sup> at room temperature with a Unicam SP 100 spectrophotometer, using KBr pellets. A 400-mg pellet contained 2 mg complex. The wavelength was checked with polystyrene. The magnetic properties were studied by the Gouy method, on a Weiss-type magnet at room temperature, with a field-strength of 6000 Gauss. The instrument was calibrated with

an aqueous solution of NiCl<sub>2</sub> [5] and with Co[Hg(SCN)<sub>4</sub>] [6].

A previously reported method [7] was followed in the calculations based on the ligandfield.

# **Results and discussion**

# Visible spectra

The visible spectra of the complexes  $[Ni(en)_3]X_2$  and  $[Ni(en)_2]Y_2$  (X = = Y = halogen) are characterized (both in the solid and in the dissolved state) by the three medium-intensity bands of hexacoordinated compounds (Fig. 1). On the basis of the octahedral model these were assigned to the transitions  ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}(v_{1}), \; {}^{3}T_{1g} \leftarrow {}^{3}A_{2g}(v_{2}) \text{ and } \; {}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}(v_{3}).$  A number of inflections can be observed, mainly on the descending sides of the  $v_1$  and  $v_2$  bands; these are probably connected with spin-forbidden transitions (Table I).

#### Table I

Spectral data for the complexes  $[Ni(en)_3]X_2$  and  $[Ni(en)_2]Y_2$  and the calculated parameters

Complex	a)	Band maxima <sup>b)</sup>				D ad	<b>D</b> (1)	( ()
		$\nu_1$	$\nu_{i,1}$	$\nu_2$	$v_3$	$-B_{35}^{c,d}$	B <sub>33</sub> c)	Co
$[\mathrm{Ni}(en)_3]\mathrm{Cl}_2$	r	11.50	13.50	18.50	29.00	867	-	_
	е	11.45	13.40	18.70	29.10	897	862	3315
[Ni(en) <sub>3</sub> ]Br <sub>2</sub>	r	11.50	13.60	18.50	29.20	880		
	e	11.35	13.40	18.50	29.20	910	862	3287
$[\mathrm{Ni}(en)_3]\mathrm{I}_2$	r	11.50	13.60	18.40	29.40	887		
	е	11.30	13.45	18.65	29.10	923	862	3248
$[Ni(en)_2]Cl_2$	r	10.20	12.00	17.10	27.10	907		
	w	11.30	12.40	18.65	29.10	857		_
	e	11.50	13.00	18.60	29.10	880	835	3171
$[\mathrm{Ni}(en)_2]\mathrm{Br}_2$	r	10.10	12.00	17.10	27.00	920		•
	w	10.90	12.50	17.70	28.30	887	-	_
	е	11.30	13.00	18.50	29.20	920	836	3032

a) r: reflection data; e: aqueous solution with 5% en excess; w: in pure water

b) in kK

c) in cm<sup>-1</sup> d)  $B_0 = 1084$  cm<sup>-1</sup>

The slight asymmetry of the bands, and the occasional weak inflection, point to the complexity of the bands (which is to be expected because of the low symmetry), but it is not possible to interpret this in the spectra measured at room temperature. The theoretical number of bands corresponding to the low symmetry cannot be detected.



Fig. 1. Reflection (a) and solution (b) spectra of  $[Ni(en)_3]Cl_2$ 



Fig. 2.  $[Ni(en)_2]Cl_2$ : (a) reflection spectrum, (b) spectrum of the aqueous solution, (c) spectrum of the aqueous solution in the presence of 5% en

It can be seen from Table I that the spectral data of the solid and dissolved complexes scarcely differ; the anion-effect is minimal. The shifts of the bands are more significant in the reflection spectra of  $[Ni(en)_2]Cl_2$  and  $[Ni(en)_2]Br_2$ , but the spectra of their aqueous solutions (even without an excess of en) are already practically identical with those of the tris complexes (Fig. 2).

The quotients  $v_2/v_1$  (and also  $v_3/v_2$ ), which can be regarded as a measure of the deviation from octahedral symmetry, differ from the ideal value of 1.80 [8, 9], being 1.60—1.65 and 1.56—1.60, respectively; the distortion of the molecules can therefore be no longer neglected. In some spectra taken at low temperature the splitting of the  $v_1$  and  $v_2$  bands can be observed, and thus the presence of the low-symmetry components is doubtless.

The parameters  $B_{35}$  and C show the characters of the bonds tending to be strongly ionic. In the variation of the  $B_{35}$  values (calculated on the basis of the Laporte-forbidden bands), the relations

$$B( ext{soln.}) > B( ext{refl.}); \ B( ext{tris}) < B( ext{bis}); \ B( ext{Cl}^-) < B( ext{Br}^-) < B( ext{I}^-)$$

can clearly be recognized. Thus, the earlier finding [10] is valid, according to which a lower ionic character arises in the crystal state as a result of the lattice effects, while in the case of the same anion the bonds forming the tris complexes are more covalent. The sequence  $Cl^- < Br^- < I^-$  corresponds to the order of polarizability of the anions; the effect of the anions in the spectra is small.

The parameter C has values in the range 3310-3250 cm<sup>-1</sup>, and the ratio C/B is 3.5-3.7 instead of the theoretical 4.

With the use of the average 10Dq,  $B_{35}$  and C values for the tris complexes (11.37 kK, 910 cm<sup>-1</sup> and 3280 cm<sup>-1</sup>), the positions were calculated for the seven intercombination bands expected theoretically, but which cannot be detected in the spectra. The positions calculated for the bands  $v_{i,1}-v_{i,7}$  are in turn 13.40, 24.40, 26.80, 28.80, 37.90, 38.20 and 60.90 kK. With the above Dq,  $B_{35}$  and C values the energies of the bands  $v_1$ ,  $v_2$ ,  $v_3$  can be recalculated with satisfactory accuracy.

The  $B_{35}$  values calculated from  $v_1 + v_2$  or from  $v_1 + v_3$  are high (larger than  $B_{ion}$ ), and in addition the trend of their change is also different, indicating that the ground and excited states are correctly described by different values of Dq, B and C.

The positions of the  $v_{i,1}$  band  $({}^{1}E_{g} \leftarrow {}^{3}A_{2g})$  in the solution spectra of the tris complexes can be quite well detected, and thus the  $B_{33}$  values [11, 12] too could be calculated. The values obtained with the formula  $E(v_{i,1}) = 16B_{33} - 6B_{33}^{2}/10Dq$  for the Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> complexes hardly differ and are smaller than the  $B_{35}$  values. It can be concluded from the  $B_{35}$  and  $B_{33}$  values that the  $\pi$ -character in the Ni–N bonds is not significant, independently of (X).

The bis complexes, with the exception of the Cl<sup>-</sup> and Br<sup>-</sup> complexes, an only be studied in the solid state. Their spectra up to 320 nm show strucures characteristic of diamagnetic, square planar complexes.

# Magnetic properties

Only the tris-(ethylenediamine) and the dihalogeno-bis-(ethylenediamine) complexes are paramagnetic; the other examined compounds of the type  $[Ni(en)_2]Y_n$  are diamagnetic. The magnetic moments measured for the complexes  $[Ni(en)_3]X_2$  in solution and in the solid state are given in Table II.

The values are characteristic of hexacoordinated nickel(II) complexes. Similarly to other complexes, e.g. those of Co(II) [13], the  $\mu_{BM}$  values increase along the series Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>. When  $\mu_{BM}$  and 10Dq are known, the spinorbital coupling constant  $\lambda$  can be calculated. It can be concluded from the constants  $\lambda$ ' calculated with the two types of relation [14, 15] that the symmetry of the NiN<sub>6</sub> group is lower than  $O_h$ . In the case of an ideally octahedral structure, or one approaching this, a value smaller than, but approximately equal to -324 cm<sup>-1</sup> should be obtained from the formula (c) in the last column of Table II.

Complex	$\mu_{BM}$		$-\lambda_{(\text{soln.})}$ and $\lambda'/\lambda_0 = \alpha^2$			
	solid	soln.a)	b)	c)		
	3.21	3.22	190 (0.59)	326 (1.01)		
$[Ni(en)_3]Br_2$	3.22	3.25	197 (0.61)	352 (1.08)		
$[Ni(en)_3]I_2$	3.30	3.34	204 (0.63)	444 (1.37)		

Table II

a) aqueous solution containing 5% en

b)  $-\lambda = \frac{0.27 B^2}{Dq}$ c)  $-\lambda = 1 - \sqrt{\frac{\mu_{BM}^2}{8} - \frac{2.085 T}{10Dq}} \cdot \frac{10 Dq}{4}$  used for the calculation

### Infrared spectra

The interpretation of the many bands in the infrared spectrum of the ligand is difficult. Reference is made to the work of SABATINI and CALIFANO [16] who report data for *en* and deuterated *en* measured in the vapour, liquid and solid states. Some characteristic frequencies for the ligand and its studied complexes are given in Tables III and IV.

Of the three conformations of *en* (*cis*, *trans* and *gauche*), the *trans* form is not suitable for complex formation. Investigations of the lattice structure [17] have indicated that, similarly to  $[Co(en)_3]^{3+}$  [18], the *gauche* form is present in the complex  $[Ni(en)_3]^{2+}$  (see also [19]).

According to POWELL and SHEPPARD [20], the spectra of hexacoordinated nickel(II)-en complexes (type B) have simpler structures (Fig. 3) than for instance those of  $[Co(en)_3]^{3+}$  complexes (type A). It is characteristic of the spectra of type B that a very intense band is to be found at about 1030 cm<sup>-1</sup>, while it is absent from spectra of type A [20, 21]. A substantial difference can also be observed in the regions 400—650 and 1250—1400 cm<sup>-1</sup>; the reason for the difference has not yet been clarified.

It can be stated that the infrared spectra of *en* and its nickel(II) complexes do not differ essentially. One of the most important regions is that of the  $\nu(NiN)$  vibrations. Numerous compilations can be found for the Ni—N stretching frequencies (e.g. [22]), but the data and band assignments reported by the individual authors differ. In the complexes  $[M(en)_2X_2]$  two  $\nu(MN)$  vibrations are infrared-active, and in the microsymmetry of square planar  $MN_4$  one  $\nu(MN)$  vibration is infrared-active.

DURIG et al. [23] give values of 430—520 cm<sup>-1</sup> for the v(MN) vibration in Pd-en complexes. If this is true, then these bands are to be expected below 500 cm<sup>-1</sup> for metals of the first transition series. The bands of the metal-N

Compound	$\nu(\mathrm{NH}_2)$	$\nu(\mathrm{CH}_2)$	$\gamma_{s}(\mathrm{NH}_{2})$	Yas(CH2)	Yas(NH2)	$\beta_{as}(\mathrm{NH_2})$	v(NiN)
en	3335	2930	1360	1305	980	647	525
	3246	2858		1298			
$[Ni(en)_3]Cl_2$	3324 s	2948 s	1329 m	1277 m	984 m	662 m	525 m
	3288 s	2880 s					
	3240 s						
	3164 s						
$[Ni(en)_3]Br_2$	3330 s	2947 s	1329 m	1277 m	982 m	660 m	525 m
	3287 s	2880 s				623 m	
	3245 s						
	3245 s						
$[Ni(en)_3]I_2$	3320 s	2940 s	1329 m	1277 m	982 w	662 m	523 m
	3282 s	2881 s				624 m	
	3240 s						
	3149 s					+	
$[\mathrm{Ni}(en)_3]\mathrm{S}_2\mathrm{O}_3$	3280*s	2918 s	1327 m	1269 m	994 m	660 m	538 m
	3168 s	2872 s					
[Ni(en)3]PtCl6 [6]	3342	2947	1332	1282	972	653	
	3292	2897				640	?
	3188					617	
$[Ni(en)_2]Cl_2$	3325 s	2952 s	1326 m	1271 m	979 m	682 m	526 m
	3290 s	2940 s					
	3120 s	2875 s					
[Ni(en),]Br,	3326 s	2960 s	1332 m	1281 m	984 m	680 m	527 m
	3296 s	2945 s					
	3255 s	2885 s					

 Table III

 Characteristic spectral data of paramagnetic nickel(II)-en complexes

s = strong, m = medium, w = weak-intensity band

\* = complex band

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Fig. 3. Infrared spectrum of  $[Ni(en)_3]Br_2$  in the range 375-4000 cm<sup>-1</sup>

Lable IV	T	able	IV
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Infra	red sp	ectral d	lata of	compl	lexes of	the	type	[N]	i(en	$)_{2}$	Y	n
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Y	$\nu(\mathrm{NH}_2)$	$\nu(CH_2)$	$\gamma_{s}(\mathrm{NH}_{2})$	Yas(CH2)	$\gamma_{as}(\mathbf{NH}_2)$	$\beta_{as}(\mathrm{NH}_2)$	$\nu(NiN)$
[Ag(CN) <sub>2</sub> ] <sup>-</sup>	3338 s 3279 s	2957 m 2910 m	1316 w	1272 w	957 m	673 w	525 w
[Zn(CN) <sub>4</sub> ] <sup>2-</sup>	3340 s	2836 m 2951 m	1318 m	1272 w	958 m	672 m	522 m
	3277 s	2914 m 2866 m				-	
[Cd(CN) <sub>4</sub> ] <sup>2–</sup>	3354 s 3294 s	2991 m 2954 m	1309 w	1271 w	957 w	638 m	518 m
		2922 m 2872 m					
[AgI <sub>2</sub> ] <sup>-</sup>	3241 s 3196 s 3092 m	2940 m	1300 w	1254 w	977 m	588 w	488 w
[CuI <sub>2</sub> ] <sup>-</sup>	3243 s 3193 s 3089 m	2942 m	1300 w	1254 w	978 m	584 m	490 w
[HgI <sub>4</sub> ] <sup>2-</sup>	3242 s 3194 s 3093 m	2938 m	1303 w	1258 w	979 m	588 w	488 w

vibration are given as about 400 cm<sup>-1</sup> in compounds of *en* with Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup>. In the case of Cr<sup>2+</sup>-*en* a value below 450 cm<sup>-1</sup> has been reported [24]. It is generally accepted that the energy of the  $\nu(MN)$  vibration in the M-*en* compounds is approximately the same, or a little less than in M-NH<sub>3</sub> complexes.

For the compounds  $[Ni(NH_3)_6]X_2$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) SACCONI *et al.* [25] give the v(NiN) band at 334, 327 and 322 cm<sup>-1</sup>, respectively, whereas in the hexamines of Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, etc. this band lies in the range 270—340 cm<sup>-1</sup>. In contrast with this, values of 520—540 cm<sup>-1</sup> are found in the complexes  $[Cu(en)_2]^{2+}$  [26].

It appears probable from the presently reported data that the band of the Ni—N stretching vibration must be in the range 500-540 cm<sup>-1</sup> for all of the compounds studied. This assignment corresponds with that reported by **POWELL** and **SHEPPARD** [20]. The spectra of the tris and the bis complexes are very similar.

A very intense band at about 400 cm<sup>-1</sup> was found by BLYHOLDER and VERGEZ [27] for  $[Ni(en)_3]Cl_2$ , and was assigned to the v(NiN) vibration; this band does not appear in the spectrum of this complex in the present measurements.

In the range 1028—1155 cm<sup>-1</sup> a characteristic band system is to be found; this is due to skeletal stretching and  $\gamma_{as}(\rm NH_2)$  vibrations. The  $\nu(\rm CH_2)$ and  $\nu(\rm NH_2)$  vibrations appear sharply at 2870—3170 and 3240—3320 cm<sup>-1</sup>, respectively.

The bis-en complexes can be stabilized both by the linear  $[Ag(CN)_2]^$ complex [28] and by the tetrahedral complexes  $[Zn(CN)_4]^{2-}$  and  $[Cd(CN)_4]^{2-}$ [29]. The  $v(C \equiv N)$  band of the complex anion is at 2159, 2150 and 2140 cm<sup>-1</sup> for the complexes  $[Ni(en)_2][Ag(CN)_2]_2$ ,  $[Ni(en)_2][Zn(CN)_4]$  and  $[Ni(en)_2]$ ,  $[Cd(CN)_4]$ , respectively, in good agreement with the values of 2164, 2149 and 2141 cm<sup>-1</sup>, respectively, for the free ions [30-32]. The spectra of the compounds isolated with the I<sup>-</sup> complexes are also markedly similar to those of the other bis complexes, and more or less agree with those reported earlier by LEVER et al. [2].

If the spectra of complex molecules of the various types are compared, several regions can be found where the difference is considerable:

(1) In the range 375—800 cm<sup>-1</sup> there are two, two, four and three medium-intensity bands for the compounds of types a, b, c and d, respectively.

(2) For the *a* type, one band-system is obtained at  $1100-1200 \text{ cm}^{-1}$ , and another at  $1570-1640 \text{ cm}^{-1}$ ; in contrast with this, the complex band at  $1100-1200 \text{ cm}^{-1}$  does not occur for the other types, while only a single band appears at  $1570-1640 \text{ cm}^{-1}$ .

(3) The spectral structures differ considerably in the range 2500-3400 cm<sup>-1</sup>. The bands between 2800 and 3000 cm<sup>-1</sup> appear most strongly in types

a and b, and have substantially lower intensities in types c and d. Above 3100  $cm^{-1}$  the  $\nu(NH_2)$  and the H<sub>2</sub>O bands for types a and b are found in the form of one wide, complex band, while for types c and d the band system is much more sharply separated (Fig. 4).



Fig. 4. Spectra in the range 2500-4000 cm<sup>-1</sup> of (1) [Ni(en)<sub>3</sub>]Cl<sub>2</sub>, (2) [Ni(en)<sub>2</sub>][Zn(CN)<sub>4</sub> (3)  $[Ni(en)_2][HgI_4]$ 

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# DEDUCTION OF THE REYNOLDS EQUATIONS OF TURBULENCE FROM THE GYARMATI PRINCIPLE

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It is shown that, similarly to the Navier – Stokes equation of viscous flow, also the Reynolds equations of turbulent flow are deducible from the GYARMATI integral principle of non-equilibrium thermodynamics. In the course of the deduction LORENTZ's dissipation potential is somewhat generalized, and it is demonstrated that the Lagrangian density in the GYARMATI principle can be split into two separate parts belonging to the mean motion and the fluctuating motion, respectively. The validity of GYAR-MATI's supplementary theorem is discussed in the case of quasi-linear constitutive equations, the variational principle is proved to remain operative in such cases, too.

### 1. Preliminaries

It is well known that the Navier—Stokes equation of viscous flow was not deducible from a variational principle for a long time. Although great efforts were made to draw up the problem within the scope of a suitable variational task [1—4], the researches — excluding some very special cases did not lead to any positive result. The negative results were characterized by SERRIN in his excellent article [5]: "Other negative results concerning variational principles yielding Navier—Stokes equation are due to GERBER [6] and BATEMAN [7]." Of course, the possibility of deducing the Reynolds equations of turbulent flow from a variational principle could not arise until the problem of derivation of the Navier—Stokes equation was solved.

In 1965 the tide was turned; starting from an alternative form of ONSAGER's principle of minimum energy dissipation [8], GYARMATI formulated the integral principle of dissipative processes [9, 10] within the framework of non-equilibrium thermodynamics. From this principle VERHÁS [11] first deduced the simple Navier—Stokes equation, then Böröcz [12] derived also the generalized hydrodynamic equation of motion belonging to the antisymmetric part of the pressure tensor and describing the internal rotation too. After these results GYARMATI wrote already in 1967 [13]: "It is evident that the Reynolds equations of turbulent flow can also be derived from the integral principle, and the situation is similar with respect to the fundamental equations of magnetohydrodynamics, plasma physics, etc."

Likewise in 1967, further significant progress was made. GYARMATI recognized that it is more favourable to formulate the integral principle in the universal form first given by ONSAGER and MACHLUP for the special case of adiabatically closed discontinuous systems [14]. The universal form of the integral principle of dissipative processes is manifoldly advantageous compared with the partial form previously used. Its main advantage lies in remaining valid in the case of quasi-linear problems, that is, when the conductivities and resistances depend on state parameters, such as temperature, concentrations, velocity, etc. This was first proved is the case of heat conduction in solids [15], then its general validity was shown by GYARMATI with the recognition of a new theorem [16]. Special examples for discussing quasi-linear problems based on the GYARMATI principle and on the supplementary theorem were given by SÁNDOR [17], for the case of multicomponent isothermal diffusion, while in case of thermohydrodynamics by the author [18]. It should be mentioned that recently NIHOUL [19] raised the problem of deriving the basic equations of turbulent flow from a variational principle, but he did not reach essential progress, because - obviously being unfamiliar with the complete literature — he negated the existence of an appropriate variational principle [17]: "Unfortunately, no such variational principle, mathematically equivalent to the Navier-Stokes equations, has yet been found for turbulence, but we may hope that a refined study of the physical insight of the phenomenon may suggest a 'thermodynamical' principle approximating satisfactorily its exact description."

In this paper it will be shown that GYARMATI's governing principle of dissipative processes is equivalent to the Reynolds equations representing the basic equations of turbulent flow, and they are deducible from the former. Starting even from the universal form of the GYARMATI principle [13, 15, 16—18] and demonstrating — so to say, as an example — the validity of the supplementary theorem, our results will remain valid for turbulent phenomena that can be described by Reynolds equations with non-constant coefficients. In short, it will be demonstrated that the GYARMATI principle is a fundamental one, not only for linear turbulent flows, but for the much more general nonlinear ones too. The incompressibility of the fluid will be used as a single simplifying assumption; this, however, does not invalidate the generality of our results.

### 2. On the Gyarmati principle

The turbulent flow of the fluid will be described by the method of classical continuum physics. The fact of turbulence will be taken into account by introducing state parameters that can be related to the statistical behaviour of the turbulent drift space. In order to deduce the Reynolds equation, we

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start from the following form of the GYARMATI principle given in energy picture

$$\delta \int_{V} \mathfrak{L} \, dV = 0 \, ; \quad \mathfrak{L} = T\sigma - \Psi - \Phi \tag{1}$$

since this is the most suitable form for describing inertial motions [12, 13, 18, 20]. Thus in Eq. (1) the Lagrangian density  $\mathfrak{L}$  is regarded as a function of the energy dissipation  $T\sigma$  (where T is the temperature and  $\sigma$  is the entropy production per unit volume and unit time) and of the dissipation potentials  $\Psi$  and  $\Phi$ . These quantities are defined with the aid of the current densities  $I_i$  and the thermodynamic forces  $X_i$  as follows:

$$T\sigma = \sum_{i} \boldsymbol{I}_{i} \cdot \boldsymbol{X}_{i}; \quad \boldsymbol{\Psi} = \frac{1}{2} \sum_{i,k} L_{ik} \boldsymbol{X}_{i} \cdot \boldsymbol{X}_{k}; \quad \boldsymbol{\Phi} = \frac{1}{2} \sum_{i,k} R_{ik} \boldsymbol{I}_{i} \cdot \boldsymbol{I}_{k}$$
(2)

For simplicity, here, a vector notation was applied, the coefficients  $L_{ik}$  and  $R_{ik}$  were, for the elements of the tensors  $[L_{ik}]$  and  $[R_{ik}]$ , respectively, submitted to ONSAGER's reciprocity relations [13]. It is important to note that in the linear theory of non-equilibrium thermodynamics, the coefficients  $L_{ik}$  and  $R_{ik}$  are considered as constants, whereas in the quasi-linear case they may depend on the state parameters (such as temperature, flow rate, etc.). In the case of transport processes such parameters can always be given from which the thermodynamic forces can be generated as gradients, that is,  $X_i \equiv \nabla \Gamma_i$ . Hence in Eq. (1) the Lagrangian density  $\mathfrak{L}$  has to be regarded as a function of the quantities  $\Gamma_i$ ,  $I_i$ ,  $\nabla \cdot I_i$  and  $\nabla \Gamma_i$ , *i.e.* 

$$\mathfrak{L} = \mathfrak{L}(\Gamma_i, \nabla \Gamma_i, I_i, \nabla \cdot I_i).$$

In the case of independent variation of parameters  $\Gamma_i$  and current densities  $I_i$ , the transport equations

$$\frac{\partial \mathfrak{L}}{\partial \Gamma_i} - \nabla \cdot \frac{\partial \mathfrak{L}}{\partial \nabla \Gamma_i} = 0 \tag{3}$$

and the constitutive equations

$$\frac{\partial \mathcal{L}}{\partial \boldsymbol{I}_i} - \boldsymbol{\nabla} \cdot \frac{\partial \mathcal{L}}{\partial \boldsymbol{\nabla} \cdot \boldsymbol{I}_i} = 0 \tag{4}$$

belong to variational principle (1) as Euler-Lagrange equations.

Our task is now to determine the Lagrangian density of (1) for the case of a one-component fluid. Disregarding the antisymmetrical part of the viscous pressure tensor  $\mathbf{P}^{v}$ , the energy dissipation can be given in the form [12, 13, 18, 20, 21]:

$$T\sigma = -p^{v} \nabla \cdot \boldsymbol{v} - \mathring{\mathbf{P}}^{vs} : (\nabla \mathring{\boldsymbol{v}})^{s} \ge 0.$$
(5)

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Here the scalar quantity  $p^v$  represents one third of the trace of the viscous pressure tensor  $\mathbf{P}^v$ ,  $\mathbf{\hat{P}}^{vs}$  is the symmetrical part of  $\mathbf{P}^v$ , v is the velocity, and  $(\nabla \hat{v})^s$  is the symmetrical part of the velocity gradient tensor  $\nabla v$ , from \_ which  $\nabla \cdot v$  is subtracted. The relations between the current densities and forces in Eq. (5) in the case of a Stokes fluid (using the energy picture) are given by the constitutive equations [5, 12, 13, 18, 20, 21]:

$$p^{v} = -L_{vv} \nabla \cdot v; \quad L_{vv} = R_{vv}^{-1} = \eta_{v}$$
  
$$\dot{\mathbf{P}}^{vs} = -L^{(tt)} (\nabla \dot{v})^{s}; \quad L^{(tt)} = R^{(tt)-1} = 2\eta$$
(6)

where  $\eta_v$  and  $\eta$  are the coefficients of bulk and shear viscosity, respectively, which are now considered independent of the state parameters. Later this restriction will be abandoned.

Taking into account constitutive equations (5) and (6), the dissipation potentials are

$$\Psi = \frac{\eta_v}{2} (\nabla \cdot \boldsymbol{v})^2 + \eta (\nabla \boldsymbol{v})^s : (\nabla \boldsymbol{v})^s \ge 0, \qquad (7)$$

and

$$\Phi = \frac{1}{2\eta_v} p^{v_2} + \frac{1}{4\eta} \mathring{\mathbf{P}}^{v_s} : \mathring{\mathbf{P}}^{v_s} \ge 0$$
(8)

using the energy picture [12, 13, 18, 19]. These forms are naturally regarded as a priori given with respect to variational principle (1).

Let now the splitting of the pressure tensor **P** be considered:

$$\mathbf{P} = p\mathbf{\delta} + \mathbf{P}^{v} = (p + p^{v})\mathbf{\delta} + \mathbf{P}^{vs}.$$
(9)

Furthermore, we use the vector analytical identity

$$\nabla \cdot (\mathbf{\dot{P}}^{v} \cdot v) = p^{v} \nabla \cdot v + \mathbf{\dot{P}}^{vs} : (\mathbf{\nabla v})^{s} + v \cdot \nabla \cdot \mathbf{P}^{v}, \qquad (10)$$

where p is the hydrostatic pressure and  $\delta$  is the unit tensor. The term  $\nabla \cdot \mathbf{P}^{\nu}$  in this identity can be expressed from the balance of momentum

$$\varrho \frac{d\boldsymbol{v}}{dt} + \boldsymbol{\nabla} \cdot \mathbf{P} = \varrho \boldsymbol{f}, \qquad (11)$$

where  $\rho$  is the mass density and f is the body force. By using now formulas (5)—(11) and applying Gauss' theorem for the term  $\nabla \cdot (\mathbf{P}^{v} \cdot \boldsymbol{v})$ , variational principle (1) can be obtained in the form

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$$\delta \int_{V} \left\{ -\boldsymbol{v} \cdot \left[ \varrho \frac{d\boldsymbol{v}}{dt} + \nabla p - \varrho \boldsymbol{f} \right] - \frac{\eta_{v}}{2} (\nabla \cdot \boldsymbol{v})^{2} - \eta (\nabla \boldsymbol{\dot{v}})^{s} : (\nabla \boldsymbol{\dot{v}})^{s} - \frac{1}{2\eta_{v}} p^{v^{2}} - \frac{1}{4\eta} \, \mathring{\mathbf{P}}^{vs} : \mathring{\mathbf{P}}^{vs} \right\} dV - \delta \oint_{\Omega} (\mathbf{P}^{v} \cdot \boldsymbol{v}) \cdot d\boldsymbol{\Omega} = 0, \qquad (12)$$

which is the exact variational principle of Navier-Stokes fluids under the restriction represented by the balance of momentum (11) [11, 12, 13, 18, 20].

# 3. The Gyarmati principle for turbulent motion

It will now be shown how expressions (5), (7) and (8) are modified by taking into account the case of turbulent motion.

To characterize the state parameters of the turbulent drift space, the mean values with respect to time and the fluctuations around these mean values will be used following the fundamental works of REYNOLDS [22] and LORENTZ [23]. As a basic assumption, it will be accepted that in the case of developed turbulence the fluctuations are small with respect to the mean values. Thus the turbulent state parameters are:

where the bars denote the respective mean values, while the dashes refer to the fluctuations. For simplicity, the mass density  $\rho$  will be considered non-fluctuating, that is, density-preserving motion will be investigated:

$$\varrho = \text{constant.}$$
(14)

Let us turn now our attention to the formulation of the GYARMATI principle for the case of turbulent motion. This can be done by substituting expressions (13) of the state parameters accounting for turbulence into form (12) of the principle valid in the laminar case. Hence we obtain the expressions of the energy dissipation (5) and of the dissipation potentials (7), (8), split into two parts: one can be assigned to the mean values of the state parameters (to the mean motion), the other to their fluctuations (to the fluctuating motion). Hence the variational principle (1) can be given as

$$\delta \int_{V} \left( \overline{\mathbb{Z}}^* + \overline{\mathbb{Z}}' \right) dV = 0, \qquad (15)$$

where

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$$\bar{\mathfrak{L}}^{*} = T\bar{\sigma}^{*} - \bar{\Psi}^{*} - \bar{\varPhi}^{*} = -\bar{p}^{v}\nabla\cdot\bar{v} - \overset{\circ}{\mathbf{P}}^{vs} : (\overset{\circ}{\nabla}\bar{v})^{s} - \frac{\eta_{v}}{2}(\nabla\cdot\bar{v})^{2} - \eta(\overset{\circ}{\nabla}\bar{v})^{s} : (\nabla\bar{v})^{s} - \frac{1}{2\eta_{v}}\bar{p}^{v2} - \frac{1}{4\eta}\overset{\circ}{\mathbf{P}}^{vs} : \overset{\circ}{\mathbf{P}}^{vs} \qquad (16)$$

is the Lagrangian density belonging to the mean motion, whereas

$$\bar{\mathfrak{L}}' = T\sigma' - \bar{\Psi}' - \bar{\Phi}' = -p^{v'} \nabla \cdot v' - \mathring{\mathbf{P}}^{vs'} : (\nabla \mathring{v}')^s - \frac{\eta_v}{2} (\nabla \cdot v')^2 - \eta (\nabla \mathring{v}')^s : (\nabla \mathring{v}')^s - \frac{1}{2\eta_v} p^{v'^2} - \frac{1}{4\eta} \mathring{\mathbf{P}}^{vs'} : \mathring{\mathbf{P}}^{vs'}$$
(17)

is that belonging to the fluctuating part, and the quantities  $\bar{\sigma}^*, \bar{\Psi}^*, \bar{\Phi}^*$  and  $\bar{\sigma}', \bar{\Psi}', \bar{\Phi}'$  have similar meanings. It has to be mentioned that the splitting of the Lagrangian density represented by Eqs (16) and (17) is a consequence of (13), (14) and of the constitutive equations (6). For example the term  $-\bar{p}^v \nabla \cdot v'$  of the energy dissipation will be cancelled out by the term  $-1/\eta_v \bar{p}^v p^{v'}$  of the dissipation potentials because of the constitutive equation  $> \eta_v \nabla \cdot v' = p^{v'}$ . The correctness of our statement can be proved similarly for other mixed terms including mean values as well as fluctuations.

As in the case of form (12) of the variational principle, the restriction derived from the balance of momentum (11) has to be taken into account now, too. However, in the case of turbulent motion we must turn from the substantial time derivative d/dt involved in the balance of momentum (11) to the substantial time derivative d/dt taken on a "particle" operating on mean velocity  $\bar{v}$  with the aid of the transformation:

$$\frac{d\boldsymbol{v}}{dt} = \frac{d\boldsymbol{v}}{dt} + \left[ (\boldsymbol{v} - \overline{V}) \cdot \boldsymbol{\nabla} \right] \boldsymbol{v} = \frac{d\boldsymbol{v}}{dt} + (\boldsymbol{v}' \cdot \boldsymbol{\nabla}) \boldsymbol{v}.$$
(18)

The situation is similar to the case of multicomponent continua with dif fusion processes, where every single component has a proper velocity field [13, 24]. Taking now into account expressions (13) and (18), the balance of momentum (11) can be split into the balance equations

$$\varrho \frac{d\overline{\boldsymbol{v}}}{dt} + \nabla \cdot (\varrho \,\overline{\boldsymbol{v}' \boldsymbol{v}'} + \overline{\mathbf{P}}) = \varrho \boldsymbol{f} \tag{19}$$

and

$$\varrho \frac{d\boldsymbol{v}'}{dt} + \nabla \cdot (\varrho \boldsymbol{v}' \ \bar{\boldsymbol{v}} + \mathbf{P}') - \varrho \bar{\boldsymbol{v}} (\nabla \cdot \boldsymbol{v}') + \varrho \boldsymbol{v}' (\nabla \cdot \bar{\boldsymbol{v}}) = 0$$
(20)

belonging to the mean and the fluctuating motion, respectively. With the aid of these balance equations and (10), the Lagrangian densities (16) and (17) can be given in the final form

$$\begin{split} \bar{\mathfrak{S}^{*}} &= -\bar{\boldsymbol{v}} \cdot \left[ \varrho \frac{d\bar{\boldsymbol{v}}}{dt} + \boldsymbol{\nabla} \cdot (p\boldsymbol{\delta} + \bar{\varrho \boldsymbol{v}' \boldsymbol{v}'}) - \varrho \boldsymbol{f} \right] - \frac{\eta_{v}}{2} (\boldsymbol{\nabla} \cdot \bar{\boldsymbol{v}})^{2} - \\ &- \eta (\boldsymbol{\nabla} \bar{\boldsymbol{v}})^{s} \cdot (\boldsymbol{\nabla} \bar{\boldsymbol{v}})^{s} - \frac{1}{2\eta_{v}} \, \bar{\boldsymbol{p}}^{v2} - \frac{1}{4\eta} \, \boldsymbol{\mathring{\mathbf{P}}}^{vs} \cdot \boldsymbol{\mathring{\mathbf{P}}}^{vs} - \boldsymbol{\nabla} \cdot (\boldsymbol{\overline{\mathbf{P}}}^{v} \cdot \bar{\boldsymbol{v}}) \,, \end{split}$$
(21)

and

$$\overline{\mathfrak{D}}' = -\boldsymbol{v}' \cdot \left[ \varrho \, \frac{d\boldsymbol{v}'}{dt} + \boldsymbol{\nabla} \cdot (\boldsymbol{p}' \, \boldsymbol{\delta} + \varrho \boldsymbol{v}' \, \overline{\boldsymbol{v}}) - \varrho \, \overline{\boldsymbol{v}} (\boldsymbol{\nabla} \cdot \boldsymbol{v}') + \varrho \boldsymbol{v}' (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}}) \right] - \frac{\eta_v}{2} (\boldsymbol{\nabla} \cdot \boldsymbol{v}')^2 - \eta (\boldsymbol{\nabla} \boldsymbol{v}')^s : (\boldsymbol{\nabla} \boldsymbol{v}')^s - \frac{1}{2\eta_v} \, \boldsymbol{p}^{v'2} - \frac{1}{4\eta} \, \boldsymbol{\mathring{P}}^{vs'} : \boldsymbol{\mathring{P}}^{vs'} - \boldsymbol{\nabla} \cdot (\boldsymbol{P}^{v'} \cdot \boldsymbol{v}') \,, \qquad (22)$$

where the term  $\overline{\rho v'v'}$  in the Lagrangian density of the mean motion is REYNOLDS's turbulent stress tensor [22, 24], while the expression

$$\Phi_{\rm turb} \equiv -\boldsymbol{v}' \cdot \left[ \varrho \boldsymbol{v}'(\boldsymbol{\nabla} \cdot \bar{\boldsymbol{v}}) - \varrho \bar{\boldsymbol{v}}(\boldsymbol{\nabla} \cdot \boldsymbol{v}') + \boldsymbol{\nabla} \cdot (\varrho \boldsymbol{v}' \, \bar{\boldsymbol{v}}) \right]$$
(23)

can be regarded as a generalization of LORENTZ's turbulent dissipation potential [23, 24]. The latter is equal to the energy dissipated from the mean motion to the fluctuating motion per unit volume and unit time.

# 4. Deduction of the Reynolds equations

Taking into consideration the Lagrangian densities (21) and (22), variational principle (15) can be given in the form

$$\delta \int_{V} \left\{ -\overline{\boldsymbol{v}} \cdot \left[ \varrho \, \frac{d\overline{\boldsymbol{v}}}{dt} + \nabla \cdot (\overline{\boldsymbol{p}} \delta + \varrho \overline{\boldsymbol{v}' \boldsymbol{v}'}) - \varrho f \right] - \frac{\eta_{v}}{2} (\nabla \cdot \overline{\boldsymbol{v}})^{2} - \eta (\nabla \widetilde{\boldsymbol{v}})^{s} : (\nabla \widetilde{\boldsymbol{v}})^{s} - \frac{1}{2\eta_{v}} \overline{\boldsymbol{p}}^{v2} - \frac{1}{4\eta} \, \overset{\circ}{\mathbf{P}}^{vs} : \overset{\circ}{\mathbf{P}}^{vs} - \boldsymbol{v}' \cdot \left[ \varrho \, \frac{d\boldsymbol{v}'}{dt} + \nabla \cdot (p'\delta + \varrho \boldsymbol{v}' \overline{\boldsymbol{v}}) - \varrho \overline{\boldsymbol{v}} (\nabla \cdot \boldsymbol{v}') + \varrho \boldsymbol{v}' (\nabla \cdot \overline{\boldsymbol{v}}) \right] - \frac{\eta_{v}}{2} (\nabla \cdot \boldsymbol{v}')^{2} - \eta (\overset{\circ}{\nabla} \boldsymbol{v}')^{v} : (\overset{\circ}{\nabla} \boldsymbol{v}')^{s} - \frac{1}{2\eta_{v}} p^{v'2} - \frac{1}{4\eta} \, \overset{\circ}{\mathbf{P}}^{vs'} : \overset{\circ}{\mathbf{P}}^{vs'} : \overset{\circ}{\mathbf{P}}^{vs'} \right\} dV - \delta \oint_{\Omega} (\overline{\mathbf{P}}^{v} \cdot \overline{\boldsymbol{v}} + \mathbf{P}^{v'} \cdot \boldsymbol{v}') \cdot d\Omega = 0, \qquad (24)$$

which represents GYARMATI's "governing principle of dissipative processes" for the case of turbulent motion. The Euler-Lagrangians belonging to the

principle will be — in correspondence to general equations (3) and (4) — the equations of the transport of momentum and the constitutive equations. In both cases two sets of equations can be distinguished, those related to the mean and the fluctuating motion, respectively.

Let the components  $\bar{v}_{\beta}$  ( $\beta = 1, 2, 3$ ) of the mean velocity  $\bar{v}$  be regarded as " $\Gamma_i$ " parameters:  $\Gamma_i \equiv \bar{v}_{\beta}$ . Then the Euler—Lagrange equation

$$\varrho \frac{d\boldsymbol{v}}{dt} + \nabla \cdot (\bar{\boldsymbol{p}} \boldsymbol{\delta} + \varrho \overline{\boldsymbol{v}' \boldsymbol{v}'}) - \varrho \boldsymbol{f} - \nabla (\eta_v \nabla \cdot \bar{\boldsymbol{v}}) - \nabla \cdot \left[2\eta (\hat{\boldsymbol{\nabla v}})^s\right] = 0$$
(25)

belonging to variational principle (24) is identical with the transport equation of momentum of the mean motion.

Regarding components  $v'_{\beta}$  ( $\beta = 1, 2, 3$ ) of the velocity fluctuation v' as " $\Gamma_i$ " parameters:  $\Gamma_i \equiv v'_{\beta}$ , the Euler—Lagrangian belonging to (24)

$$\varrho \frac{d\boldsymbol{v}'}{dt} + \nabla \cdot (p' \,\delta + \varrho \boldsymbol{v}' \boldsymbol{\bar{v}}) - \varrho \boldsymbol{\bar{v}} (\nabla \cdot \boldsymbol{v}') + \varrho \boldsymbol{v}' (\nabla \cdot \boldsymbol{\bar{v}}) - \nabla (\eta_v \nabla \cdot \boldsymbol{v}') - \nabla \quad 2\eta \, (\nabla \boldsymbol{\hat{v}}')^s ] = 0$$
(26)

is equal to the transport equation of momentum of the fluctuating motion. Naturally, variational principle (24) has to be considered by varying the quantities  $\bar{v}_{\beta}$  and  $v'_{\beta}$  simultaneously but independently of each other. In a sense similar to the independent variation of the current densities of momentum  $\bar{p}^{v}$ ,  $\hat{\bar{\mathbf{P}}}^{vs}$ ,  $p^{v'}$ ,  $\hat{\mathbf{P}}^{vs'}$ , the constitutive equations

$$\frac{1}{\eta_v} \overline{p}^v + \nabla \cdot \overline{v} = 0; \qquad \frac{1}{\eta_v} p^{v'} + \nabla \cdot v' = 0;$$

$$\frac{1}{2\eta} \mathring{\mathbf{P}}^{vs} + (\nabla v)^s = 0; \qquad \frac{1}{2\eta} \mathring{\mathbf{P}}^{vs'} + (\nabla v')^s = 0$$
(27)

belong to the general system of Euler-Lagrangians given in Eq. (4).

The "natural boundary conditions" belonging to variational principle (24) are

$$[\eta_{v} \nabla \cdot \bar{\boldsymbol{v}} + \bar{\boldsymbol{p}}^{v}]_{n} = 0; \qquad [\eta_{v} \nabla \cdot \boldsymbol{v}' + \boldsymbol{p}^{v'}]_{n} = 0; \qquad (28)$$
$$[2\eta(\nabla \hat{\boldsymbol{v}})^{s} + \mathring{\bar{\boldsymbol{P}}}^{vs}]_{n} = 0; \qquad [2\eta(\nabla \hat{\boldsymbol{v}}')^{s} + \mathring{\boldsymbol{P}}^{vs'}]_{n} = 0;$$

where n is the external normal of the boundary surface  $\Omega$ .

By considering the viscous coefficients independent of the space coordinates, and both the mean and the fluctuating motions incompressible, transport equations (25) and (26) are reduced to the Reynolds equations commonly used:

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$$\varrho \frac{d\overline{\boldsymbol{v}}}{dt} + \nabla \cdot (\overline{\boldsymbol{p}} \boldsymbol{\delta} + \varrho \overline{\boldsymbol{v}' \boldsymbol{v}'}) - \eta \Delta \overline{\boldsymbol{v}} - \varrho \boldsymbol{f} = 0$$
<sup>(29)</sup>

and

$$\varrho \frac{d\boldsymbol{v}'}{dt} + \nabla \cdot (p' \boldsymbol{\delta} + \varrho \boldsymbol{v}' \overline{\boldsymbol{v}}) - \eta \varDelta \boldsymbol{v}' = 0.$$
(30)

Thus GYARMATI's "governing principle of dissipative processes" is proved to be equivalent to the corresponding equations of motion even in the case of turbulent phenomena.

### 5. Quasi-linear constitutive equations

It will be shown as a further generalization that the GYARMATI principle can be regarded as an exact integral principle for turbulent phenomena even in the general and practically important case when in constitutive equations (6) the viscosity coefficients depend on the hydrostatic pressure, velocity and possibly on the temperature. In the latter case the distribution of temperature is supposed to be uniform in the fluid, but it has to be mentioned that, based on our former work [18] these results can be further generalized to non-isothermal turbulent systems.

With the aim of discussing the above case let us consider GYARMATI's supplementary theorem, which guarantees the validity of variational principle (1) even in case of so-called quasi-linear constitutive equations, that is, when the coefficients depend on state parameters.

The supplementary theorem asserts that the variation of the dissipational potentials (2) with respect to state parameters  $\Gamma_i$  vanishes in real processes, *i.e.* 

$$\delta_{\Gamma_j}(\Psi + \Phi) = \sum_j \frac{\partial(\Psi + \Phi)}{\partial \Gamma_j} \delta \Gamma_j = 0$$
(31)

is valid. However, the  $L_{ik}$  and  $R_{ik}$  coefficients may depend on parameters  $\Gamma_j$  [15, 16, 17, 18].

Following GYARMATI's reflections, the validity of the supplementary theorem will now be proved — so to say as an example — for the case of turbulent phenomena with non-constant coefficients.

Taking into account Eqs (16) and (17), theorem (31) can be given in the detailed form:

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$$\begin{split} \delta_{\overline{\boldsymbol{v}}} \bigg[ \frac{\eta_{v}}{2} (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^{2} + \frac{\eta_{v}}{2} (\boldsymbol{\nabla} \cdot \boldsymbol{v}')^{2} + \eta (\boldsymbol{\nabla} \hat{\overline{\boldsymbol{v}}})^{s} : (\boldsymbol{\nabla} \hat{\overline{\boldsymbol{v}}})^{s} + \eta (\boldsymbol{\nabla} \hat{\boldsymbol{v}}')^{s} : (\boldsymbol{\nabla} \hat{\boldsymbol{v}}')^{s} : (\boldsymbol{\nabla} \hat{\boldsymbol{v}}')^{s} + \\ &+ \frac{1}{2\eta_{v}} \overline{\boldsymbol{p}}^{v2} + \frac{1}{2\eta_{v}} \mathbf{P}^{v'2} + \frac{1}{4\eta} \,\overset{\circ}{\mathbf{P}}^{vs} : \overset{\circ}{\mathbf{P}}^{vs} + \frac{1}{4\eta} \,\overset{\circ}{\mathbf{P}}^{vs'} : \overset{\circ}{\mathbf{P}}^{v} \\ \delta_{\boldsymbol{v}'} \bigg[ \frac{\eta_{v}}{2} (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^{2} + \frac{\eta_{v}}{2} (\boldsymbol{\nabla} \cdot \boldsymbol{v}')^{2} + \eta (\overset{\circ}{\boldsymbol{\nabla}} \hat{\boldsymbol{v}})^{s} : (\overset{\circ}{\mathbf{\nabla}} \hat{\boldsymbol{v}}) + \eta (\overset{\circ}{\boldsymbol{\nabla}} \hat{\boldsymbol{v}}')^{s} : (\overset{\circ}{\mathbf{\nabla}} \hat{\boldsymbol{v}}')^{s} + \\ &+ \frac{1}{2\eta_{v}} \overline{\boldsymbol{p}}^{v2} + \frac{1}{2\eta_{v}} \boldsymbol{p}^{v'2} + \frac{1}{4\eta} \,\overset{\circ}{\mathbf{P}}^{vs} : \overset{\circ}{\mathbf{P}}^{vs} + \frac{1}{4\eta} \,\overset{\circ}{\mathbf{P}}^{vs'} : \overset{\circ}{\mathbf{P}}^{vs'} \bigg]. \end{split}$$

Similar expressions are obtained for the variation with respect to all state parameters (temperature, pressure, etc.) on which the coefficients  $\eta_v$  and  $\eta$ may depend. (Obviously the validity of the theorem for state parameters of homogeneous distribution — as, in our case, for temperature — or for ones whose gradients do not cause irreversible processes — such as hydrostatic pressure — is trivial [18].)

With the aim of proving the actual form (32) of the theorem, let the parts related to the bulk viscosity of the mean motion be remoted from Eq. (32). Then there follows expression

$$\frac{1}{2} \left[ \frac{\partial \eta_v}{\partial \overline{\boldsymbol{v}}} \, (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^2 + \left( \frac{\partial}{\partial \overline{\boldsymbol{v}}} \, \frac{1}{\eta_v} \right) \overline{\boldsymbol{p}}^{v^2} \, \right] \delta \overline{\boldsymbol{v}} + \frac{1}{2} \left[ \frac{\partial \eta_v}{\partial \boldsymbol{v}'} \, (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^2 + \left( \frac{\partial}{\partial \boldsymbol{v}'} \, \frac{1}{\eta_v} \right) \overline{\boldsymbol{p}}^{v^2} \, \right] \delta \boldsymbol{v}' \tag{33}$$

or after some reduction

$$\frac{1}{2} \frac{\partial \eta_v}{\partial \overline{\boldsymbol{v}}} \left[ (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^2 - \frac{1}{\eta_v^2} \overline{\boldsymbol{p}}^{v^2} \right] \delta \overline{\boldsymbol{v}} + \frac{1}{2} \frac{\partial \eta_v}{\partial \boldsymbol{v}'} \left[ (\boldsymbol{\nabla} \cdot \overline{\boldsymbol{v}})^2 - \frac{1}{\eta_v^2} \overline{\boldsymbol{p}}^{v^2} \right] \delta \boldsymbol{v}' \quad (34)$$

which vanishes because of the second constitutive equation in (27). It can be demonstrated in a similar way that the variations of the other terms in Eq. (32) also vanish in a real process, that is, when the fluxes and forces of the field of flow are connected by constitutive equations of the type (27). Recently, the GYARMATI theorem has been generalized by FARKAS and NOSZTICZIUS for nonlinear constitutive equations much more general than the linear (or in case of non-constant coefficients quasi-linear) ones in (27) [26]. It is remarkable that our results are easily generalizable also for non-isothermal turbulent systems by taking into account our former paper related to hydrothermodynamics [18].

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# COMPRESSIBILITÉ DES SOLUTIONS AQUEUSES DE CERTAINS HALOGENURES, I

## CHLORURES DES MÉTAUX ALCALINS

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Pour déterminer les valeurs des compressibilités adiabatiques des solutions aqueuses de chlorure de lithium, chlorure de sodium et chlorure de potassium, on a mesuré la vitesse de propagation des ultrasons, par la méthode de diffraction de lumière monochromatique sur un faisceau ultrasonique.

On a envisagé et comparé la variation de la compressibilité avec la température et la concentration dans des conditions identiques pour toutes les solutions mentionnées. Les variations constatées sont attribuées aux modifications structurales et aux interactions électriques spécifiques des solutions étudiées.

Le caractère adiabatique du processus de propagation des ondes ultrasoniques permet de déterminer, mesurant la vitesse de propagation, quelques constantes caractéristiques des différents milieux. Ces constantes sont particulièrement utiles dans les recherches effectuées pour établir les liaisons entre certaines propriétés moléculaires [1]. A l'aide de cette méthode simple et précise on peut évaluer l'effet de la concentration et celui de la température sur les grandeurs suivantes: coefficients de compressibilités adiabatique et isothermique, chaleur spécifique à volume constant, certaines constantes caractéristiques des ions se trouvant dans les solutions, etc. [2, 3].

C'est dans cette optique, que le présent travail traite la variation de la compressibilité adiabatique avec la concentration, la température et les propriétés du cation, dans le cas des solutions aqueuses de LiCl, NaCl et KCl.

On a varié la concentration à partir de 0,2 M jusqu'au voisinage de la concentration de saturation (y compris l'eau distillée) dans l'intervalle de températures de  $15^{\circ}$ —50 °C.

Le coefficient de compressibilité adiabatique a été déterminé à l'aide de la relation suivante:

$$eta_{
m ad} = rac{1}{arrho v^2}$$

où:  $\rho$  est la densité de la solution et v la vitesse de propagation des ultrasons dans la solution. Les valeurs des densités étant connues [4], la vitesse a été mesurée par la méthode de diffraction de lumière monochromatique dans un champ ultrasonique [5].

# **Résultats** experimentaux

La compressibilité adiabatique des solutions de LiCl en fonction de la température, à concentration constante, est présentée sur la fig. 1. L'élévation de la température diminue les valeurs  $\beta_{ad}$  de façon identique à celle de ce qu'on constate dans l'eau.



Fig. 1. Variation de la compressibilité adiabatique des solutions aqueuses de LiCl avec la température

La tendance de diminution des pentes avec la hausse de la température, de même que la réduction des valeurs:  $\partial \beta_{ad} / \partial t$  avec l'augmentation de la concentration sont évidentes.

Le domaine de températures étant limité jusqu'à 50 °C, le point de la compressibilité minimale et la partie ascendante de la courbe:  $\beta_{ad} = f(t)$  n'ont pas été mis en évidence dans le cas de l'eau. Les modifications des coefficients de température de la compressibilité avec la concentration entraînent cependant l'existence des minima. A mesure que la concentration augmente, ils se déplacent vers les valeurs de températures plus faibles. A partir de la concentration de 6 M les minima se situent dans l'intervalle de température recherchée et à 10 M le minimum se place à 40 °C environ.

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Dans les solutions de NaCl et de KCl, la variation des compressibilités avec la température (voir fig. 2 et 3) ne présente pas de différences qualitatives par rapport à celles de la solution de LiCl. Jusqu'au minima on constate alors la diminution des valeurs de  $\beta_{ad}$  avec la température; on peut également remarqué qu'avec l'augmentation de la concentration les gradients de température des compressibilités diminuent. Le déplacement des minima vers les températures moins élevées en augmentant la concentration, entraîne l'apparition de ceux-ci dans l'intervalle poursuivie, à partir de 2 *M* pour NaCl et de 1 *M* pour KCl.



Fig. 2. Variation de la compressibilité adiabatique des solutions aqueuses de NaCl avec la température

Fig. 3. Variation de la compressibilité adiabatique des solutions aqueuses de KCl avec la température

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Comme on peut le constater, les minima représentant les points d'inversement du sens de la variation de la compressibilité avec la température, s'installent pour chaque électrolyte à différentes valeurs de températures et de concentrations. A la même concentration, les températures des minima de compressibilité décroissent avec l'augmentation du poids moléculaire du sel.

La diminution des pentes des courbes de compressibilité avec l'augmentation de la concentration indique la réduction progressive de l'effet de l'agitation thermique et la tendance à atteindre la compressibilité indépendante de la température.



Fig. 4. Variation de la compressibilité adiabatique des solutions aqueuses de LiCl avec la concentration

Fig. 5. Variation de la compressibilité adiabatique des solutions aqueuses de NaCl avec la concentration

Les trois solutions présentent des analogies pour les variations de la compressibilité avec la concentration à la température constante. Les figures 4, 5 et 6 indiquent les comportements des solutions de LiCl, NaCl et KCl.

On remarque la diminution de  $\beta_{ad}$  avec la concentration et les courbes pour les dilutions plus élevées deviennent droites. Les intersections indiquant les valeurs de  $\beta_{ad}$  communes pour deux valeurs de températures à une concentration donnée, est la conséquence de l'existence des points symétriques par rapport à la position des minima mentionnées. La convergence des courbes de températures différentes vers les concentrations plus élevées résulte du fait que la variation de la compressibilité avec la température se trouve diminué, lorsque la concentration augmente.

Les trois électrolytes ayant le même anion mais des cations différents, présentent des compressibilités distinctes parmi les conditions identiques de température et de concentration. Les courbes de la figure 7 illustrent ce comportement à t = 30 °C. Il en est de même pour les autres valeurs de températures dans l'intervalle étudiée.

A mesure que le rayon des cations augmente, les compressibilités diminuent systématiquement et en même temps remarque-t-on l'augmentation des différences  $\Delta\beta_{ad}$  pour les électrolytes mentionnées, avec la croissance de la concentration.







Fig. 7. Variation des compressibilités adiabatiques des solutions aqueuses de: LiCl,NaCl, KCl avec la concentration

## Interprétation des résultats

Les valeurs des compressibilités adiabatiques des solutions aqueuses étudiées résultent des conditions d'équilibre des différents éléments structurals soumis à l'agitation thermique et aux interactions électrostatiques. Les variations des compressibilités avec la température, la concentration de la solution et le rayon des cations, mises en évidence dans le présent travail, reflètent les déplacements du système vers les nouveaux états d'équilibre déterminés par la modification des rapports des intensités des interactions mentionnées.

Le solvant (dans le cas présent l'eau) subit sous l'action de l'agitation thermique deux effets de sens contraire. Ainsi les modifications de la compressibilité adiabatique s'expliquent par le déplacement de l'équilibre de la structure tétraédrique à celle semblable au quartz dus aux ruptures des liaisons hydrogène, ou bien à la dilatation thermique. A mesure que l'une ou l'autre de ces deux actions prédomine, la compressibilité varie en un sens ou l'autre.

La dissolution des sels dans l'eau impose au système de nouveaux états d'équilibre, dus à la complexité de facteurs qui exercent des influences réciproques. En premier lieu, le changement de concentration des substances à poids moléculaires différents, influence les valeurs des compressibilités par l'intermède de la densité. Ce fait est mis en évidence par la diminution de la compressibilité avec la croissance de la concentration. La présence de ions dans le solvant modifie la structure de ce dernier à la suite de la rupture des liaisons hydrogène. Cet effet s'ajoute à celui d'analogue à l'agitation thermique et contribue au déplacement de l'équilibre vers les structures plus compactes, ayant une compressibilité plus faible, proportionnellement à la croissance du nombre d'ions dans la solution.

Les données obtenues relatives à la variation de la compressibilité avec la concentration vérifient la relation suivante [6]:

$$\beta_{\rm ad} = \beta_0 + AC + BC^{3/2}$$

Pour les concentrations petites cette relation devient:

$$\beta_{\rm ad} = \beta_0 + AC$$

où  $\beta_0$  représente la compressibilité adiabatique de l'eau.

Pour ces raisons et en conséquence des interactions électrostatiques (qui sont en équilibre dynamique avec l'agitation thermique) la contribution de l'élévation de la température sur les modifications structurales est limitée aux valeurs inferieures à celles de l'eau.

A côté des interactions électrostatiques, les ions agissent en même temps par leur charge sur les molécules du solvant, en augmentant leur moment dipolaire et modifiant par conséquence la constante diélectrique en proportion inverse avec la distance de l'ion. C'est la raison pour laquelle les molécules polaires orientées du solvant agissent à leur tour sur les ions changeant leur énergie potentielle électrostatique. Il est évident que la force de ces interactions dépende du nombre et de la nature des ions en solution. Cela se reflète dans la variation de la compressibilité avec la concentration et les propriétés des ions correspondants. L'agitation thermique intervient en sens inverse sur l'effet mentionné, de façon à freiner l'orientation des dipoles du solvant.

Les champs électriques des ions agissent sur les molécules du solvant produisant des effets d'électrostriction de différents degrés, proportionnels au nombre des ions et en proportion inverse avec leurs rayons.

Les couches extrêmement condensées des enveloppes d'hydratation des ions de la solution contribuent également au changement de la compressibilité, conformément aux concentrations d'ions en solution dans la mesure des degrés d'hydratation des ions [7, 8]. L'anion des sels employés étant identique, les différences trouvées sont dues aux cations. Les courbes présentées dans la figure 7 montrent que la compressibilité adiabatique augmente avec la diminution des rayons des cations, c'est-à-dire l'augmentation du degré d'hydratation. C'est en désaccord avec la constatation qui vient d'être mentionnée plus haut. La contradiction s'explique par le fait que l'apport de la densité accrue, augmentant la compressibilité de la solution, est bien plus grand que celui du degrés d'hydratation qui agit en sens inverse [9, 10].

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La variation des valeurs de  $\beta_{ad}$  en fonction de la densité établit l'ordre prévu des courbes, les compressibilités étant proportionnelles aux rayons des cations, par suite de la variation correspondante des degrés d'hydratation et du nombre des ions.

## Conclusions

1. La compressibilité adiabatique des solutions aqueuses des chlorures de lithium, sodium et potassium se trouve diminuée lorsque la concentration augmente.

2. La variation de la compressibilité avec la température dans les solutions aqueuses étudiées est analogue à celle de l'eau pure et présente des minima qui se déplacent vers les valeurs plus petites de température avec la croissance de la concentration.

3. Si l'anion des sels est le même dans tous les cas, les compressibilités dépendent des propriétés du cation de la solution.

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# ELECTROSTATIC THEORIES FOR THE INTERPRETATION OF THE FORMATION OF MIXED COMPLEXES

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A study was made of the electrostatic theories of KIDA, and of MARCUS and ELIÉZER interpreting the formation of mixed complexes. It is pointed out that KIDA's interpretation takes into account only the atomic radii and neglects all other factors. From calculations on the mixed complexes HgBrI and FeFCl<sup>+</sup> and with the use of literature data, it has been shown that the electrostatic stabilization energy calculated on the basis of the MARCUS and ELIÉZER models amounts to about one ten-thousandth of the total energy of interaction. The reliability of this otherwise low value is further decreased by the possible change of other factors (e.g. bond distance, bond angle, etc.). According to the models, the energies calculated for the individual complex species do not follow the measured equilibrium constants even qualitatively, and indeed the existence of HgF<sub>2</sub> in aqueous solution would be justified. With the use of literature data, difficulties are pointed out in the calculation of the dielectric constant of the solvent.

The large number of mixed complexes, and also the fact that mixed complexes are formed transitionally in numerous reactions, make particularly noteworthy all those theories which attempt to interpret the extent of formation of mixed complexes. On the basis of electrostatic considerations and models, KIDA [1], and then MARCUS and ELIÉZER [2], explained and calculated the stability constants of mixed complexes. Although the authors elaborated their theories not only for the simplest mixed complexes of type MAB, we considered it sufficient to limit ourselves to a treatment of these.

# Interpretations of the stabilities of mixed complexes according to Kida, and Marcus and Eliézer

As regards the factors determining the stabilities of mixed complexes, both KIDA [1], and MARCUS and ELIÉZER [2], deal with essentially the same ones as those discussed by BJERRUM [3] in interpreting stepwise equilibrium constants. According to this, the logarithm of the ratio of two stepwise stability constants (log  $K_n K_{n,n+1}^{-1} = T_{n,n+1}$ ) can be given as the sum of the logarithm of the ratio of stability constants calculable on the basis of statistical considerations ( $S_{n,n+1}$ ) and the logarithm of the stability constant ratio calculable from the ligand effect ( $L_{n,n+1}$ ):

$$T_{n,n+1} = S_{n,n+1} + L_{n,n+1} \tag{1}$$

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The first term expresses the probability of binding of the ligand, while according to BJERRUM, the ligand effect is made up of two terms: the electrostatic effect (its logarithm is  $E_{n,n+1}$ ), and the rest effect (its logarithm is  $R_{n,n+1}$ ). As regards the nature of these two latter effects,  $E_{n,n+1}$  arises from purely Coulombic interaction ( $\varphi$ ) and its value is:

$$E_{n,n+1} = 0.4343 \frac{\varphi_{n,n+1}}{kT}$$
(2)

where k is the Boltzmann constant, and T is the temperature in  $^{\circ}$ K. In those complexes where the coordination sphere is occupied by uncharged ligands, the electrostatic energy is zero, and so the logarithm of the value of the rest effect arises from the difference in the logarithms of the constants measured experimentally and calculated statistically.

On this basis, KIDA [1] studied the electrostatic energy change occurring during mixed complex formation, and showed that if, for example, a square planar mixed complex,  $trans-MA_2B_2$ , is formed from the square planar parent complexes,  $MA_4$  and  $MB_4$ , then the repulsion energy between the anions in the mixed complex will be smaller than (or the same as) half the sum of the repulsion energies between the anions in the two parent complexes. Since the energy of attraction does not change, an electrostatically more stable (or just as stable) product comes about, and this means, therefore, that the formation of the mixed complex from the corresponding parent complexes is favoured.

KIDA also made similar considerations with other types of complexes, and regarded the difference in the logarithms of the measured stability constant and the statistical formation constant as a measure of the extra stabilization.

In developing the theory of KIDA, MARCUS and ELIÉZER [2, 4, 5] accurately calculated the extent of the electrostatic energy change on the formation of mixed complexes and then, essentially on the basis of the Bjerrum formula, represented the logarithm of the stability constant of a mixed complex as the sum of three terms:

$$\log K_M = \log K_{\text{stat}} + \log K_{el} + \log K_R \tag{3}$$

where  $K_{\text{stat}}$  is the statistical formation constant,  $K_{el}$  can be calculated from the electrostatic interaction, and  $K_R$  represents the remaining interactions. MARCUS and ELIÉZER did not publish data with regard to the size of  $K_R$ ; they merely noted that until the solvent effect could be calculated explicitly it would be included in this [3].

In order to be able to calculate as accurately as possible the energy difference arising from the electrostatic interaction during the formation of the

mixed complex, MARCUS and ELIÉZER put forward two electrostatic models. According to both models, the molecules of both the mixed and the parent complexes are built up from rigid, spherical ions, and both the elementary charges, z, of the ions, and the dipoles induced in the individual ions, are at their centers.

Compared with the first model [2], which takes into consideration only the ion-ion and ion-dipole interactions, the second [4, 5] means an advance from two points of view: firstly, the field strengths at the centers of the individual ions can be calculated more exactly, and secondly the interactions between the dipoles and the energy of formation of the induced dipoles are also taken into account. Since these predominantly have destabilizing effects, the second model appears suitable for the interpretation of the stabilities of mixed complexes less stable than expected on statistical grounds. On the basis of both the first and second model, MARCUS and ELIÉZER calculated values in excellent agreement with the experimentally obtained data.

#### **Calculations on mixed complexes MAB**

Using an abridged formula, MARCUS and ELIÉZER calculated the energy difference arising during mixed complex formation; in this way, however, it is not possible to obtain a picture of the size of the energies of individual interactions. The aim of our calculations was the elucidation of these, and principally the determination of the size of the destabilizing interactions. From among the complexes studied by MARCUS and ELIÉZER, we made calculations only on the mixed complex mercury(II) bromide iodide; apart from this, we made de-

Mixed complex	Interatomic distances	Polarizabilities	Dipole moments
HgBrI	$d_{ m Hg-Br}=2.41~ m \AA$	$\alpha_{Hg^{2+}}=2.45\!\times\!10^{-24}~cm^3$	$\mu_{\rm Br-} = 6.86 \ \rm D$
	$d_{ m Hg-I}~=2.59~ m \AA$	$\alpha_{\rm Br-}~=4.97\!\times\!10^{-24}~{\rm cm^3}$	$\mu_{\rm I-}$ = 8.22 D
		$\alpha_{I-} ~= 7.55 \!\times\! 10^{-24}~{\rm cm}^3$	$\mu_{\rm Hg^{2+}} = 0.34  {\rm D}$
			$\mu_{\rm Br-} = 6.60 \ \rm D$
			$\mu_{\rm I-}$ = 8.53 D
FeFCl+	$d_{ m Fe-F}~=~2.03~ m \AA$	$\alpha_{\rm F^{-}} = 0.98 \times 10^{-24} \ {\rm cm^3}$	$\mu_{\rm F-}$ = 3.05 D
	$d_{ m Fe-Cl}~=~2.52$ Å	$\alpha_{Cl-} = 3.53 \times 10^{-24} \text{ cm}^3$	$\mu_{\rm Ci-} = 6.96  {\rm D}$
			$\mu_{\rm F-}$ = 3.05 D
			$\mu_{\rm Cl-} = 6.95 \ {\rm D}$

Table I

Constants used in the calculations based on the electrostatic models

Complex	Energy of ion-ion interaction	Energy of ion-dipole interaction	Energy of dipole–dipole interaction	Energy of induced dipole	Electrostatic energy of the complex
	$+e^2  {Z_M  Z_A \over d} = +1912.03$	$+e \; rac{Z_M  \mu_A}{d^2_A} = +1133.71$	$+2  \frac{\mu A M}{d_A^3} = +34.79$	$-\frac{\mu^2 A}{2\alpha_A} = -473.31$	
	$+e^2rac{Z_M Z_B}{d_B}=+1779.15$	$+e \; rac{Z_M  \mu_B}{d_B^2} = +1176.10$	$-2  rac{\mu B \; \mu M}{d_B^3} = -33.58$	$-rac{\mu^2 B}{2lpha_B}=-447.27$	
	$-e^2  {Z_A  Z_B \over D} = -  460.80$	$+e \; rac{Z_A \; \mu_M}{d^2_A} = + \; 29.34$	$-2 \frac{\mu A \ \mu B}{D^3} = -90.19$	$-rac{\mu^2 M}{2lpha_M}=-2.57$	
HgBrI		$-e \; rac{Z_B  \mu_M}{d_B^2} = - \; 25.40$			
		$-e \; rac{Z_A \; \mu_B}{D^2} = - \; 157.79$			
		$-e \; \frac{Z_B  \mu_A}{D^2} = - \; 131.69$			
	total: $+3230.38$ ( $+76.14\%$ )	total: $+2024.27$ (+47.71%)	total: $-88.98$ ( $-2.10\%$ )	total: -923.15 (-21.76%)	-4242.52
	$+e_2rac{Z_MZ_A}{4d_A}=-1912.03$	$+e \; rac{Z_M  \mu'_A}{d_A^2} = +1091.20$	$-rac{\mu^2_A}{(2d_A)^3}=-38.92$	$-rac{\mu A^2}{2lpha_A} = -438.48$	
$1/2~{\rm HgBr}_2$	$-e^2  rac{Z_A^2}{4 d_A} = -  239.00$	$-e \; rac{Z_A \; \mu'_A}{2 d_A} = - \; 136.40$			
	total: +1673.03 (+77.80%)	total: +954.81 (+44.40%)	total: -38.92 (-1.81%)	total: -438.48 (-20.40%)	+2150.43
	$+e^2rac{Z_MZ_B}{d_B}=+1779.15$	$+e {Z_M\mu_B\over d_B^2} 2=+1220.42$	$-\frac{\mu B^2}{(2d_B)^3} = -52.32$	$-\frac{\mu B}{2\alpha_B} = -481.61$	
$1/2~{\rm HgI}_2$	$-e^2rac{Z_B^2}{ed_B}=-~222.39$	$-e \frac{Z_B \mu_B}{(2d_b)^2} = -152.55$		D	
	total: $+1556.76$ (+74.46%)	total: $+1067.87$ (+51.10%)	total: -52.32 (-2.50%)	total: $-481.61$ ( $-23.04\%$	+2090.70
$\Delta E$	+0.59	+1.60	+2.26	-3.06	1.36

Complex	Energy of ion-ion interaction	Energy of ion- dipole interaction	Energy of dipole-dipole interaction	Energy of induced dipole	Electrostatic energy of the complex
(FeFCl)+	+5641.41 (+82.38%)	+2412.64 $(+35.23%)$	-45.10 (0.66%)	-1161.20 (16.96%)	+6847.75
$1/2(FeF_2)^+$	+3121.18 (+86.46%)	+977.37 (+27.07%)	-13.9 (-0.39%)	-474.78 (-13.16%)	+3609.87
1/2(FeCl <sub>2</sub> )+	+2514.28 (+77.67%)	+1445.46 (+44.65%)	-37.77 ( $-1.17\%$ )	$-684.96 \\ (-21.16\%)$	+3237.01
$\varDelta E$	+5.95	-10.19	+6.74	1.46	+0.87

 Table III

 Electrostatic energy (10<sup>14</sup> erg/molecule) of the mixed complex FeFCl<sup>+</sup> according to the second model of MARCUS and ELIÉZER

tailed calculations on the mixed complex FeFCl<sup>+</sup>, a complex with characteristically ionic bonding. There is the possibility of an interesting comparison between the data obtained for this latter compound and those for the considerably more covalently bonded mixed complex HgBrI. (It should be noted that, to the best of our knowledge, the formation constant of the mixed complex FeFCl<sup>+</sup> has not so far been determined.)

In Table I are given the data used in our calculations. Of the values relating to HgBrI, only the value put forward for the polarizability of Hg<sup>2+</sup> and the interatomic distances were reported by MARCUS and ELIÉZER. The values for the polarizabilities of the bromide and iodide ions were taken from the literature [6]. Since the solvent effect can be regarded as implicitly included in the polarizability value to a certain extent, it is likely that the above authors calculated with other values. The data for the iron(II) fluoride-chloride system were also taken from the literature [6]. All of the dipole moments are values calculated from the data given in Table I.

In Tables I and II are shown the data of our calculations on the systems  $HgBr_2$ — $HgI_2$ , and  $FeF_2^+$ — $FeCl_2^+$ , respectively. The per cent values of the individual energies, referred to the electrostatic energies of the complexes, are given in brackets.

### Discussion

1. According to KIDA's interpretation, the extent of formation of the mixed complex is determined merely by the sizes of the atomic radii; *i.e.* it completely disregards the interactions arising from the difference in the electronic structures of the ions. If the interatomic distances M-A and M-B are denoted by  $d_A$  and  $d_B$ , respectively, then the electrostatic stabilization energy due to the formation of the linear mixed complex MAB is:

$$\Delta E_{el} = e^2 \left[ \frac{1}{4d_A} + \frac{1}{ed_B} - \frac{1}{d_A + d_B} \right] \tag{4}$$

It can be seen that if  $d_A = d_B$ , then  $E_{el}$  is zero, and if  $d_A \neq d_B$ , then  $\Delta E_{el}$  is always positive.

2.1. From the data in Tables II and III, which were obtained on the basis of the second model of MARCUS and ELIÉZER, it can be seen that the destabilizing terms represent considerable energies: the destabilization is about 20% of the total interactions. Thus it would be justified to expect the model to be suitable for the interpretation of the stability of mixed ligand complexes formed in amounts lower than the statistical. Nevertheless, the reliability of the model becomes uncertain if the relation of the total energies and the stabilization energies are examined. In the calculation for the HgBr<sub>2</sub>—HgI<sub>2</sub> system, the stabilization energy of  $1.4 \times 10^{-14}$  erg per molecule is the difference of energies amounting to about  $12,000 \times 10^{-14}$  erg, and this is hardly more than one ten-thousandth of the energies considered.

This relatively very small energy already in itself makes the reliability of the model very uncertain. It is known that in the case of ionic compounds, where the use of the electrostatic model itself is much more justified, the calculated and experimentally measured energies agree within 5-10%. As the authors also indicate, in the case of the mercury(II) halides a considerable covalency must be considered, and this decreases the extent of agreement attainable.

In addition to this, we must still point out certain omissions, the extents of which are small, but of an order of magnitude similar to that of the stabilization energy.

The polarizability values used for the calculations are only average values, and the polarizability is not directly proportional to the change of the field strength. As a result its values are different in the mixed ligand complex and in the parent complexes. For this reason the values of the energies connected with all the dipoles also change.

Although not likely in aqueous solutions of the mercury(II) halides, in the case of other complex systems it can readily be conceived that the A-M-B bond angle of the mixed complex molecule assumes a value different from that expected on the basis of the configurations of the parent complex molecules. The extent of this is very difficult to predict and the prevailing conditions must be taken into consideration. By this means, however, a considerable change takes place in the value and direction of the field strengths. For information, we calculated the change in the energy of the HgBr<sub>2</sub> molecule arising only from an ion-ion interaction, as a function of the Br-Hg-Br bond angle. Our results have shown that in the vicinity of 180° the model is rather insensitive to changes in the bond angle; a difference of about 7° here causes an

energy change of  $1 \times 10^{-14}$  erg per molecule. At about  $120^{\circ}$ , where a change in the angle is definitely expected, the same energy change results from a difference of only  $0.5^{\circ}$ .

It is clear that only to a first approximation can the mixed ligand complex be considered as built up from two half parent complexes; *i.e.*, it is by no means certain that some change does not take place in the bond distances during mixed complex formation. We have found that if the Hg—I distance in the mixed complex HgBrI is decreased from 2.59 Å to 2.58 Å, then the change in the stabilization energy arising from the ion-ion interactions amounts to  $0.9 \times 10^{-14}$  erg.

2.2. In the interpretation of the extent of mixed complex formation in benzene, ELIÉZER assumed that both the molecules of the parent complexes and those of the mixed complexes formed have tetrahedral configurations. He calculated the electrostatic stabilization energy according to the first model. The results of the calculations are in excellent agreement with the experimental data; this is surprising in view of the crudeness of the approximation.

It is improbable that the configurations of all the complex species are the same in benzene. In a subsequent paper [6] ELIÉZER himself remarked that in dioxan for example it is necessary to consider the repulsion between the mercury(II) halides and the methylene groups of the coordinated dioxan molecules; the size of this repulsion is affected by the nature of the halogen atom. If this is so in dioxan, then no matter how different the coordination of benzene, here too it is necessary to consider repulsion forces varying with the halogen atoms. As a result, angular distortions are to be expected upon the formation of the mixed complexes and, as we have shown, the effects of these cannot be neglected by any means.

The tetrahedral configuration assumed is also questionable from another aspect. In the interpretation of the dipole moments of the mercury(II) halides measured in dioxan, ELIÉZER [6] showed that if the HgCl<sub>2</sub> · OR molecule (OR = dioxan) is taken as planar with bond angles of 120°, then the molecule would have a dipole moment of about 5 D; in fact the experimental value is only 1.43 D. In benzene too a value of only 1.23 D was measured, and this makes the tetrahedral structure unlikely, as the latter would involve a value larger than 5 D. The question is clearly decided by the results of LE FévRE *et al.* [7]: from vapour pressure measurements on benzene solutions of mercury(II) chloride, the molecular weight of HgCl<sub>2</sub> was found to be 490  $\pm$  100; this indicates the presence of dimeric and trimeric molecules which the authors assumed to be of planar configurations. Taking these facts into consideration, it is evident that the excellent agreement between the calculated and found stabilization constants can hardly be considered as other than chance coincidence.

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In connection with the effect of the coordinated solvent molecules, ELIÉZER points out that benzene is not an inert solvent towards the mercury(II) halides, and further that the interactions with the solvent molecules in benzene and in dioxan result in a deviation of the molecular configuration from linear. On the basis of the available data it is not possible to decide the extent of the deviation from linearity. However, this by no means implies that in the case of any solvent the presence of solvent molecules in the coordination sphere can be disregarded, as was done by MARCUS and ELIÉZER in their calculations. On the basis of our own results [8] for example, in DMSO and in DMF HgI<sub>3</sub><sup>-</sup> has configurations very close to tetrahedral, whereas in water [9] and in the crystalline state it is practically planar. In the case of HgI<sub>3</sub><sup>-</sup> we assume a very strong coordination of the DMSO or of the DMF at the fourth apex of the tetrahedron, and this explains the deviation of the molecule from planarity.

2.3. The  $\beta_2$  values of the parent complexes are known from the literature (HgBr<sub>2</sub>: 2.14×10<sup>17</sup> [10]; HgI<sub>2</sub>: 6.61×10<sup>23</sup> [11]). From the known formation constant of the mixed complex (12.6 [12]), the  $\beta_2$  value of the mixed complex  $\beta_2 = ([MAB]/[M] \times [A] \times [B])$  can be calculated with the use of the following formula:

$$K = \frac{(\beta_2, \text{HgBrI})^2}{(\beta_2, \text{HgBr}_2) \times (\beta_2, \text{HgI}_2)}$$
(5)

Its value is  $1.335 \times 10^{21}$ .

From a comparison of these stability products and the electrostatic energies of the individual parent complexes and the mixed complex (Table II), two contradictions appear. Firstly, the stability constants of the individual complex species are spread over a range of about 6 orders of magnitude, whereas the differences of the calculated electrostatic energies are within one order of magnitude. Secondly, there is even a qualitative relation between the calculated and the measured stability constants; the order of the latter is  $HgI_2 > HgBrI > HgBr_2$ , the exact opposite of the order of the calculated constants. In addition, on the basis of the electrostatic model the electrostatic energy of  $HgF_2$  does not differ from those of the other mercury(II) halides, that is this too is a high positive value, although an interaction of the mercury(II) ion with fluoride ion in water was not observed.

A comparison of the data in Tables II and III also shows that the polarization ionic model cannot, even to a first approximation, take into account the extent of covalency of the bond and the bond strength increase arising from this. This is also pointed out by MARCUS and ELIÉZER in their very thorough and valuable review of the chemistry of mixed complexes [13].

2.4. From the point of view of the calculations the value of the dielectric constant of the medium is decisive. Without any justification, the authors take

the dielectric constant of the medium equal to one, and in the calculations with this value, they obtain constants in good agreement with the experimental data.

BJERRUM [14], in his theoretical interpretation of the dissociation constants of polybasic acids, has calculated values in agreement with the experimental data; nevertheless he considered calculations with the dielectric constant of the solvent (D) to be improper.

INGOLD [15] has pointed out that, as a result of the electrostriction of the solvent and the orientation and deformation of the solvent molecules, in the vicinity of the ionic charge the dielectric constant assumes a totally different value; theoretically, these effects can be taken into consideration only with great difficulty. INGOLD deemed it correct to carry out the calculations not with D but with its value multiplied by a factor k. (k is a number less than unity, corresponding to a complicated function of the distance r between the two acidic groups, which at high values of r approaches unity.)

SCHWARZENBACH [16] has reached conclusions similar to those of BJERRUM, but has shown that the INGOLD modification is not correct either. SCHWARZENBACH considered it necessary to take into account still more factors, such as the shielding effect of the acid molecule itself on the ionic charges. The solvent molecules penetrate between the acidic groups, and in such a case the effect of the dielectric constant is greater than when, as a result of the positions of the two functional groups, this possibility is restricted or nonexistent. SCHWARZENBACH found that a correct value is given by the relation  $1/d^{(1-x)}D^xk$ , in which k has the same meaning as in the INGOLD formula, d expresses something similar ("so etwas") to the dielectric constant of the acid molecule, and x is a number smaller than unity, the extent of shielding of the two ionic charges. A small x value reflects a considerable shielding, while a large x value means only slight shielding.

In his calculations of the repulsive force between iron(II) and iron(III) ions, LAIDLER [17] likewise pointed out the difficulties connected with the calculation of the dielectric constant of water. He has shown that in the vicinity of an ion the dielectric constant of water varies depending on the distance: in the case of an ion with a charge of +2, up to about 2.5 Å its value is 1.78, but after this a very considerable increase follows and atabout 6 Å it is already 70. The situation is much more complicated if wo ions are involved, since here the two fields are superimposed; this affects the dielectric constant, and this in turn the individual field strengths. Such a calculation is also made difficult by the fact that both ions extend in space. Taking this into account by an approximation procedure, the authors made calculations, the results of which, although approximate, are nevertheless better than those obtained with the full dielectric constant of the solvent, and which are probably not far from the real value.

In the case of mercury(II) halides even more complicated interactions must be taken into account, since the value of the dielectric constant must be studied in the fields of charges which are not all of the same kind.

As can be seen from the above, the value taken for the dielectric constant is an extremely difficult point in the reliability of the calculations. In this case, if its value is not 1, but 2, 3 etc., the calculated log  $K_{el}$  value for the mixed complex HgBrI is not 0.148, but 0.074, 0.05, etc., which means a considerable difference from the measured values.

2.5. In our opinion, the main value of the work of MARCUS and ELIÉZER is the demonstration that, in principle, it follows even from the very approximate electrostatic model that the stability of the mixed ligand complex can be both smaller and greater than the value obtained from statistical considerations. At the same time, however, this method of treatment also threw light on the limitations of the electrostatic model. Our present knowledge does not permit even an approximate estimation of the stability constants of mixed ligand complexes on the basis of extra-thermodynamic data.

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# NEW ROUTES FOR THE SYNTHESIS OF POLYMETHYLENEIMINES

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Possible new and economical syntheses of higher cycloimines (with 7, 8 or 9membered ring) were studied from the corresponding lactams, and a survey of the variants is given. Octahydroazocine (heptamethyleneimine), the most significant member of this group from the pharmacochemical point of view, was chosen as a model compound. A proposed new and economic synthesis of this compound, also realizable on industrial scale, consists in the NaBH<sub>4</sub> reduction of oenantholactim O-methyl ether in aqueous medium buffered by organic acids. The possibilities of preparation and hydrogenation of bis (lactimino) ethers were also studied.

Several researchers have attempted the synthesis of octahydroazocine [1-7], but before the application of metal hydrides [8], only conversions amounting to per cent could be realized. RUZICKA *et al.* [9] reduced oenantholactam in ethereal solution with lithium aluminium hydride and attained a yield of 65-70%. Lithium aluminium hydride, however, cannot be replaced by other hydride anion donors, and the use of LiAlH<sub>4</sub> is expensive and hazard-ous; therefore, the industrial application of RUZICKA's method is strongly restricted.

In search for a more advantageous preparation of octahydroazocine, we arrived at the conclusion that, in order to enhance reducibility, the lactamlactim tautomerism must be shifted to the lactim side. As shown by the infrared spectrum, in the substantial lactam the equilibrium is strongly shifted in favour of the lactam form. In a number of experiments, the carbonyl group of the lactam form was found non-reducible. Several possibilities may be utilized for a stabilization of the lactim form (e.g., formation of lactim acyl ester, lactimide, lactimide halide, etc.). Of these, the preparation of a lactim ether proved to be suitable. In the presence of a strong dehydrating agent, oenantholactam (II) is capable of forming a lactim ether (III) by itself. On the other hand, it is known from the literature [10, 11] that lactim ethers can be prepared with alkylating agents.

In the former case, the dehydrating agent  $(PCl_5, P_2O_5)$  acting as a Lewisacid may also catalyze a Beckmann rearrangement. Thus, one may obtain the bis(lactim) ether (III) from cycloheptanone oxime (I) in one single step. According to our experiences, the bis(lactim) ether (III) can then be converted by catalytic hydrogenation at high temperature and under high pressure to octahydroazocine (IV) in 25-30% yield [12].



Suitable methods are known for the preparation of lactim alkyl ethers, mainly the methyl ethers [13]. Lactim methyl ethers with low-membered rings can be saturated to polymethyleneimines under conditions under which the corresponding lactam cannot be reduced at all.

Such a catalytic way of the preparation of heptahydroazepine has been reported [14].

In a similar way, though not at all economically, we synthesized octahydroazocine [15].

PORUBSZKY et al. [16] obtained octahydroazocine (IV) by the electrolytic reduction of oenantholactim methyl ether (V), but the conversions remained below 25-30%.

It was found by BROWN et al. [17, 18] and slightly earlier by KOLLONITSCH et al. [19] that the combination of alkali borohydrides with aluminium, calcium, etc. halides in diethylene glycol alkyl ethers gives non-hazardous systems with a very strong hydrogenating activity similar to that of lithium aluminium hydride. By the use of this method, which involves the very cumbersome isolation of the product, we succeeded in attaining yields between 50 and 60% in the reduction of oenantholactim methyl ether [15]. The actual reducing agents are in this case, too, the aluminium and calcium borohydrides formed *in situ*, which are, however, unstable at room temperature.

It is known that sodium borohydride is also unstable in acid medium, yielding decomposition products of different reducing power (diborane, nascent hydrogen, etc.). In the presence of mineral acids this decomposition runs too vigorously towards molecular hydrogen. We found, however, that in homogeneous aqueous systems of low temperature and buffered with organic acids, the decomposition process can be well controlled and utilized for our
purposes. By this modification it is possible to reduce oenantholactim methyl ether to octahydroazocine on industrial scale, by a simple technology, and in excellent 90-94% yields.



Yields: 1: 25-30%; 2: 50-60%; 3: 90-94%

This method can also be applied to the reduction of lactim methyl ethers with low-membered rings, such as the production of heptahydroazocine from caprolactim methyl ether.

The chemical, economical and industrial advantages of the method can be seen from a relatively recent paper [21] which describes the conversion of the lactam by triethoxonium fluoroborate into lactim ether fluoroborate, and subsequently the reduction of this product in an anhydrous solvent with alkali borohydride in a yield of 70 to 75%.

#### Experimental

#### Bis cenantholactim ether (III) from cycloheptanonoxime

To a suspension of 208 g (1.0 mole) phosphorus pentachloride in 200 ml anhydrous toluene, a solution of 127.2 g (1.0 mole) cycloheptanonoxime in 200 ml anhydrous toluene was added dropwise at 75°C in 3 hrs., under stirring. The mixture was cooled to 20°C, poured onto 100 g of ice lumps and mixed intimately. After separation, the aqueous phase was made alkaline ( $p_H$  8.5) with ammonium hydroxide at a temperature below 25°C, under stirring. A light yellow crystalline product precipitated, which was filtered off and recrystallized from hot acetone to yield 91 g (77%) of **III**, m.p. 80–81°C [4].

#### Catalytic reduction of bis(oenantholactim) ether

118.1 g (0.5 mole) bis(oenantholactim) ether (III) was dissolved in 1100 ml anhydrous ethanol, and an ethanolic suspension of 5 g Raney nickel previously mixed with 0.2 g anhydrous copper sulfate was added to the solution. The mixture was stirred for 8 hrs. under a hydrogen pressure of 65 atm. at 130 °C inner temperature in a 5-litre heated hydrogenating autoclave equipped with a stirrer. After cooling, the catalyst was removed by filtration, and the ethanol was evaporated. The basic residue was subjected to fractional distillation at 25 torr. Octahydroaccine was collected between 68 and 74 °C at 25 torr to obtain 54.8 g (48.4%) of IV. On continuing the distillation, oenantholactam was recovered at 175—182 °C at 25 torr.

Octahydroazocine:  $n_D^{\circ}$ : 1.4733; m.p. of the hydrochloride 178 °C; m.p. of the hydrobromide 191—193 °C; m.p. of the picrate 146—148 °C.

#### Method A

#### Octahydroazocine (IV) from cenantholactim methyl ether (V)

To a solution of 141.2 g (1.0 mole) oenantholactim methyl ether in 250 ml diethylene glycol monomethyl ether 46.3 g (1.25 mole) sodium borohydride was added in small portions under stirring, at a rate to maintain the inner temperature of the mixture between 38 and 40 °C. Subsequently, a solution of 50.0 g (2 moles) of aluminium chloride hexahydrate in 250 ml of diethylene glycol monomethyl ether was added. During this procedure, the temperature of the mixture could be allowed to rise to 60-65 °C. Stirring was continued at this temperature for 4 hrs., then 100 ml of water was added by drops, and stirring was continued at 65-70 °C for 6 hrs. After cooling, a distillation attachment was affixed to the device, and the contents of the flask was distilled at reduced pressure (20 torr) until the temperature of the vapours attained 120 °C. The distillate was acidified to  $p_{\rm H}$  3 with hydrochloric acid, and the solvents evaporated at 10 torr. The residue was dissolved in 100 ml of water and the solution was made alkaline ( $p_{\rm H}$  9) with a solution of sodium hydroxide. The organic phase was separated and extracted with four 400 ml portions of diethyl ether. The combined extracts were dried, the solvent was evaporated, and the residue distilled at 20 torr. Octahydroazocine: b.p. at 20 torr: 56-65 °C; yield: 64.6 g (57%);  $n_D^{20}$ : 1.4732; m.p. of

Octahydroazocine: b.p. at 20 torr: 56-65 °C; yield: 64.6 g (57%);  $n_D^{20}$ : 1.4732; m.p. of the hydrochloride: 178-179 °C.

#### Method B

A solution of 141.2 g (1.0 mole) oenantholactim methyl ether in 200 ml of water was mixed with a solution of 110 g tartaric acid in 300 ml water at a temperature below 10 °C, under stirring. The homogeneous solution was cooled to 2 °C, and a solution of 60.5 g (1.6 mole) sodium borohydride in 400 ml water was added during 2 hrs., maintaining an inner temperature not higher than 6 °C. After completing the addition, stirring at room temperature was continued for 1 hour, and then at 100 °C for another hour. The mixture was cooled, made alkaline with 140 g (3.5 moles) of sodium hydroxide, and the separated organic phase extracted consecutively with  $1 \times 300$  and  $2 \times 150$  ml of benzene.

After removing the solvent by distillation, octahydroazocine was distilled in the way specified under Method A, to yield 100.5 g (90.15%) of **IV**.

#### Heptahydroazepine from caprolactim methyl ether

A solution of 72 g citric acid in 250 ml water was added at or below 10 °C, under stirring, to a mixture of 127.1 g (1.0 mole) caprolactim methyl ether and 200 ml water. The solution was cooled to 2 °C, then a solution of 60.5 g sodium borohydride in 400 ml water was added during 1 hr., keeping the inner temperature below 6 °C. After the addition, the mixture was stirred at room temperature for 1 hr., then at 100 °C for another hour. After cooling, the mixture was made alkaline with 140 g sodium hydroxide, and the separated organic phase extracted with  $3 \times 200$  ml of benzene. The solvent was removed by evaporation, and the residue distilled at atmospheric pressure; b.p. at 760 torr: 132–138 °C; yield: 90.1 g (90.3%); n<sub>D</sub><sup>20</sup>: 1.4642; m.p. of the picrate: 144 °C.

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### INVESTIGATIONS IN THE FIELD OF SOLID STATE **POLYMERIZATION, XXVIII\***

#### INVESTIGATION OF IODINE INITIATED SOLID STATE OLIGOMERIZATION OF ACENAPHTHYLENE **KINETICS AND MECHANISM OF THE REACTION\*\***

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The kinetics, mechanism and conditions of the oligomerization of crystalline acenaphthylene, initiated by iodine vapour were investigated. The activation energy of the overall reaction having a linear kinetic character is 28 kcal/mol. The  $\overline{DP}$  of products obtained by this way is 3-6, their iodine content being much lower than 1 iodine atom per oligomer molecule. The reaction takes place by an ionic mechanism. Presumably, the elementary reaction of initiation involves the formation of a donoracceptor complex between iodine and acenaphthylene followed by its dissociation into ions.

If high energy radiation is used for the initiation of solid state polymerization, the centers starting the kinetic chains are formed over the whole bulk of the monomer. The reacting system — at least in the first period of the reaction — can be considered as homogeneous and the variation of the dose rate permits kinetic investigations. As opposed to this, in the case of chemical initiation of solid state polymerization processes, a series of confusing circumstances must be taken into account, thus e.g. the phase of the two-component system formed by the monomer and initiator or catalyst and its change during the reaction [1]. Nevertheless, in clearing up the mechanism of a solid state reaction the latter method has the advantage of unambiguously defined active centers, whereas in the case of high energy initiated reactions the simultaneous formation of ions, radicals and excited molecules must be taken into account.

Investigating the solid state polymerization of N-vinylcarbazole, the anomaly of its spontaneous polymerization in the presence of carbon tetrachloride has been noticed [2], which can be considered as the first observation on polymerization due to the formation of charge-transfer complexes. Presumably, the strong molecular interaction in charge transfer complexes may lead to new recognitions both in the laws of solid state polymerization and the structure of the polymers thus formed.

\* Part XXVII: HARDY, GY. and NYITRAI, K.: Magy. Kém. Foly. 75, 182 (1969). \*\* Presented at the IUPAC International Symposium on Macromolecular Chemistry, Budapest, August 25-30, 1969.

Taking the above principles as a starting point, we began to investigate the iodine initiated solid state oligomerization of acenaphthylene. The iodine initiated liquid phase polymerization has been studied by a number of authors and found cationic in character [3]. Particularly interesting are the publications of SAKURADA *et al.* [4] and GIUSTI *et al.* [5, 6], who have dealt with the iodine initiated polymerization of styrene,  $\alpha$ -methylstyrene and acenaphthylene in dichloroethane and have reached different conclusions about the mechanism of the reaction. By studying the solid state reaction, we hoped to obtain data permitting to choose the more probable of the two assumptions.

#### Experimental

#### Materials

Acenaphthylene (a puriss. quality product of Schuchardt, München) has been recrystallized twice from methanol before starting the experiments. To check whether the solvent has any effect on the oligomerization, a smaller amount was recrystallized from toluene. M.p. of the monomer was found to be 92-92.5 °C; its density 1.178 g/ml (from crystallographic calculations 1.183 g/ml), both values differing greatly from the 0.899 g/ml given in the literature [7].

Iodine (puriss., Reanal product) was sublimated twice, then stored over phosphorus pentoxide. Reanal p.a. quality benzene and chloroform were used as solvents; the precipitating agent was methanol distilled (b.p. 64-66 °C) from a technical grade product. 1,2-Dichloroethane and *n*-heptane (puriss., Reanal) used as solvents in the liquid phase oligomerization and spectrophotometric experiments were first distilled then passed through a drying column filled with "Klinosorb-4" molecular sieve.

The bromine solution in glacial acetic acid was prepared from 96% acetic acid ("Erdőkémia" product), which was left to stand in a refrigerator until solidification, then the liquid was separated. It contained 5 g of sodium acetate and 50 g of bromine per liter. The 85%acid used was a p.a. product of "VEB Laborchemie Apolda". All other materials and solutions correspond to the usual analytical requirements.

#### Methods

Three methods seemed to be possible for carrying out solid state oligomerization. The melting of acenaphthylene together with iodine had to be rejected because of the explosive polymerization of the system near the melting point. A similar phenomenon has been observed by BERTHELOT in 1866 when he established the polymerization of styrene in the presence of crystalline iodine [8]. The mixing of the crystals of iodine and acenaphthylene was not suitable, because oligomerization could not be made predominant among the other simultaneous reactions. Therefore, initiation by iodine vapour had to be chosen. Oligomerization was carried out in a rimmed cylindrical glass vessel (height 8 cm, diameter 2.3 cm), by placing on its bottom a layer of crystalline acenaphthylene of known, approximately constant weight (1.40 g). After suspending a small glass vial containing iodine over the crystalline layer, the system was closed and p laced into a constant temperature bath (accuracy  $\pm 0.2$  °C).

The oligomer could not be extracted with cold methanol, because most of the products of the simultaneous side reaction were also insoluble in methanol. For this reason, the reaction mixture was dissolved in benzene in a few preliminary experiments but then chloroform was found to be more appropriate for this purpose. Before precipitating the oligomer with methanol, the by-products possibly present and insoluble in chloroform were separated on a G4 glass filter. Sodium chloride in methanol was added to the colloidal solution formed upon precipitation to promote its coagulation. The product was collected on a G4 glass filter, washed thoroughly by methanol and dried at room temperature until constant weight.

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The liquid state oligomerization experiments were carried out in closed test tubes with 0.5 mol/l of the monomer and 0.015 mol/l of iodine. With dichloroethane as solvent the oligomers were precipitated by pouring the mixture into methanol, containing benzoquinone, while in the case of *n*-heptane the product spontaneously separated from the solution. For better comparison, the progress of the reaction was followed gravimetrically. The molecular weight of the oligomers was determined cryoscopically. With the aid of known standards (cholesterol,  $\alpha$ -nitroso- $\beta$ -naphthol, benzophenone, acenaphthylene) the accuracy of the latter has been found to be  $\pm 10\%$ . All measurements were carried out in high purity benzene. In one case, the weight average molecular weight has been checked by vapour pressure osmometry with a Mechrolab 301 A type instrument.

The combustion method was used for determining the iodine content of the oligomers. To promote perfect combustion, sugar was added to the material weighed into an ash-free paper cup, which was placed afterwards into a platinum basket and combusted in an oxygen atmosphere. The combustion products were absorbed in 0.2 N sodium hydroxide, then the iodine and hypoiodite ions were oxidized to iodate by a solution of bromine in glacial acetic acid. The excess bromine was reduced by formic acid and, after acidification of the solution, potassium iodide was added and the iodine formed was tirated by 0.1 n thiosulfate in the presence of starch. By determining the iodine content of iodoform, the accuracy of the method has been found to be  $\pm 2\%$ . Because of the very low iodine content of the oligomer, the actual error of the determination is much higher but, in our opinion, does not exceed  $\pm 10\%$ .

The spectropho tometric measurements in the UV and visible range were carried out on a "Spectromom 202" type instrument with 1 cm quartz cells at  $\pm 3$  °C, using *n*-heptane as solvent. The latter or its solution with one of the components has been used for reference.

During the experiments care has been taken to minimize the exposure to light of the reaction mixture, the product obtained and particularly its solution. It is known that the benzene solution of poly-acenaphthylene undergoes degradation [9, 10] when illuminated by light.

#### **Results and discussion**

As has been established in our experiments, oligomers are formed from crystalline acenaphthylene under the influence of iodine or iodine vapour. The light yellow product melts with decomposition in the temperature range 210-217 °C. Its infrared spectrum corresponds to those of poly(acenaphthylenes) obtained by other methods [11, 12]. However, the UV spectrum differs from that described in the literature, therefore, it will be discussed in a forthcoming paper.

In the kinetic investigation of the oligomerization, difficulties were encountered owing to the side reactions occurring simultaneously in the system. With iodine vapour as initiator, although the side reactions were strongly suppressed, the presence of their products had a disturbing effect on the reaction and even more on the properties of the oligomers obtained.

It has been established that beside oligomerization at least two reactions take place in the system. The product of one of these is a sparsingly soluble low-molecular crystalline material with an iodine content below 1%. However, it shows an intense fluorescence even in a very diluted solution. Because of its poor solubility it could not be purified and thus has no sharp m.p., melting at 260-275 °C. It is probably identical with the dimer, containing one double bond, which has been investigated by DOLINSKY and DZIEWONSKY [13]. Possibly this product includes some cyclic tri- and tetramers.

The other parallel reaction resulted a black, powder-like material which seemed to be completely amorphous and opaque under the microscope. It had an iodine content of 15-16%, showed no change when heated up to 36 °C and was insoluble in all common solvents.

According to the X-ray powder patterns, it is an iodinated oligo- or polymer with a grain size and ordered structure similar to those of the oligomers.



Fig. 1. Conversion vs. time curves for solid state oligomerization at 20, 40, 50, 60 and 70 °C

It has to be mentioned that a similar product is formed from the crystalline complex of acenaphthylene with trinitrobenzene when treated by iodine vapour. Under suitable experimental conditions the main product can be separated from both of the by-products.

The conversion vs. time curves for the solid state oligomerization at 20, 40, 50, 60 and 70 °C are shown in Fig. 1. The curves are S-shaped, the induction period is followed by a nearly linear section over a wide range of conversions and the curves tend to a limit much less than 100%. This latter fact has been observed while investigating the solid state polymerization of acenaphthylene, initiated by high energy radiation or chemically with azo-bisisobutyronitrile [11, 14]. This shape of the curves, however, is not the consequence of the nature of the reaction itself but is due to the experimental method used. At time t = 0, when the system is inserted into the constant temperature bath, the initiator (iodine) is not yet in contact with the monomer but reaches its surface only after some time and penetrates slowly into the crystalline layer. The time necessary for iodine to reach the surface of the acenaphthylene, and the rate of diffusion in it, have been determined at 60 °C. By taking this into account, the kinetic data obtained at 60 °C are transformed into the curve

shown in Fig. 2, which starts from the origin with a completely linear character and subsequently reaches a limiting value. The rate corresponding to the linear section is also slightly altered: instead of the originally measured 22.0%/hr, a value of 19.6%/hr has been obtained, the difference being less than 6%.

Because of technical reasons, the dead time and diffusion rate values necessary for transforming the curves obtained at temperatures other than



Fig. 2. 1: Conversion vs. time curve at 60 °C, as determined originally. 2: Conversion vs. time curve after correction for the dead time and the rate of diffusion

60 °C have not been determined but it can be assumed that with these corrections the calculated curves would be linear. By comparing the activation energy of iodine diffusion in air and in crystalline materials with that of the oligomerization (see below), the difference between the rates of polymerization measured on the linear section of the transformed and original curves at lower temperatures can be established to be probably even smaller than the value given above. Hence, as first approximation, the rate values measured on the linear sections of the curves seen in Fig. 1 have been accepted for the characterization of the reaction.

The mathematical description of the kinetic curves — because of the complicated system — can only be formal, therefore this has been disregarded. However, it seems to be desirable to characterize the dependence of the rate of reaction on the temperature in some way. Supposing that even at lower temperatures the iodine comes into contact with all those sites of the acenaphthylene surface which may have an active role in the initiation, a logarithmic plot of the rates measured at the linear section against the reciprocal temperature would yield an overall activation energy. The corresponding Arrhenius diagram is shown in Fig. 3, the activation energy thus calculated is

28 kcal/mol. The data read from Fig. 1 together with the calculated ones are collected in Table I.

The monotonous increase of the conversion limits as a function of the temperature is significant but the value for 70 °C is considerably lower than that for 50 and 60 °C. This fact can be explained by the phenomenon also observed during the experiments that at this temperature the acenaphthylene iodine two-component system, having reached a certain iodine concentration,



Fig. 3. Arrhenius curve from the reaction rates

melts and from this time the reaction takes place in an entirely different way from that in the solid state.

The cryoscopic method has been used to determine the number average molecular weights of the oligomers. The  $\overline{DP}$  values were found to lie in the range of 3 to 6. There was no correlation between the molecular weight and the

(°C)	W (%/hr)	max %	$\frac{1000}{T} \\ 0(K-1)$	lg W
20	0.084	13	3.413	-1.076
40	0.56	17	3.195	-0.252
50	4.1	48	3.096	0.613
60	22.0	50	3.003	1.342
70	46.2	29	2.915	1.665

 Table I

 Kinetic data for the iodine initiated solid state oligomerization of acenaphthylene

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reaction temperature or the former and the conversion. The molecular weights of the oligomers obtained at different temperatures and the corresponding conversions are listed in Table II. In the case of one sample, beside the number average  $(\overline{M}_n)$ , both the weight average  $(\overline{M}_w)$  and the Z-average  $(\overline{M}_z)$  molecular weights were determined by means of vapour pressure osmometry, lightscattering and the ultracentrifuge method:

$$egin{array}{lll} \overline{M}_n = & 758 \pm & 10 \ \overline{M}_w = & 800 \pm & 80 \ \overline{M}_z = & 1400 + & 400 \end{array}$$

Because of the relatively poor accuracy of these values there was no reason for calculating the polydispersity for such low molecular weights.

From the kinetic investigation of solid state oligomerization the following can be established:

(1) Within the accuracy of the experimental method the reaction obeys linear kinetics; the conversion tends to a limit much lower than 100%, depending on the applied temperature.

(2) The overall activation energy of oligomerization is 28 kcal/mol.

(3) The average degree of polymerization for the oligomers is 3-6. Since the  $\overline{DP}$  value does not seem to be related to either the conversion or the temperature, it provides no further information about the nature of the reaction.

For clarifying the mechanism of oligomerization the similarities between the solid and liquid phase reactions have been studied. The latter was investi-

70 °C			60 °C				50 °C			40 °C		
Mol. weight	Deg. pol.	Conv. (%)	Mol. weight	Deg. pol.	Conv. (%)	Mol. weight	Deg. pol.	Conv. (%)	Mol. weight	Deg. pol.	Conv (%)	
620	4.0	6.1	550	3.6	4.0	650	4.3	16.5	860	5.6	5.8	
790	5.2	15.5	800	5.3	14.6	630	4.1	34.7	730	4.8	9.0	
830	5.5	26.5	750	5.0	14.9	530	3.5	39.7	800	5.2	11.7	
780	5.1	28.2	1010	6.7	30.0	540	3.6	44.4	550	3.6	14.8	
850	5.6	28.3	590	3.9	48.4	530	3.5	46.2	590	3.9	16.1	
			758*	5.0	50.6	550	3.6	46.6	570	3.7	17.0	
			724	4.8	52.2	560	3.7	48.0				

#### Table II

Molecular weights of products obtained in iodine initiated solid state oligomerization of acenaphthylene at different temperatures and conversions

\* determined by VPO method

gated in detail by the two research groups mentioned in the introduction [4, 6], who obtained the same results but reached different conclusions as to the mechanism of the reaction.

SAKURADA et al., like GIUSTI et al., have found the iodine initiated polymerization of styrene in dichloroethane kinetically similar. They have established that the conductivity of the reaction mixture remains at the initial low value during the entire process of polymerization and increases only after having reached 100% conversion, and also that the application of an electric field does not influence the rate of the process or the properties of the product formed. GIUSTI et al. made similar observations also for acenaphthylene but SAKURADA et al., investigating  $\alpha$ -methylstyrene, found different results. In the latter case the application of an electric field increases the rate of polymerization together with the molecular weight of the product.

SAKURADA et al. consider the process as ionic. In their opinion, the first step of initiation is the addition of iodine to styrene, resulting in the formation of an ion pair, which dissociates into free ions in a reversible process characterized by a dissociation constant. The polymerization reaction can be initiated by both the ion pair and the free ions, naturally at different rates. Based on this assumption, the above authors propose a kinetic scheme with the corresponding mathematical description, which contains two different elementary reactions each for the chain propagation, transfer and termination steps. According to their views, the different degrees of dissociation of the various monomers are responsible for their different behaviour under the influence of an electric field. If the degree of dissociation is high, the effect of the electric field is pronounced. In the case of a low degree of dissociation the field has no visible effect on the reaction, i.e. the factor which represents the change of the degree of dissociation is close to unity.

GIUSTI et al. do not agree with the above assumption. In their opinion, the different behaviour of the various monomers is caused by their entirely different mechanisms of polymerization. They consider the polymerization of  $\alpha$ -methylstyrene to be cationic, whereas those of styrene and acenaphthylene are regarded as pseudo-cationic, a term introduced by GANDINI and PLESCH [16]. According to their experience, the reaction is strongly influenced by hydrogen iodine, which, as a co-catalyst, reduces or eliminates the induction period. In their view, the first step of the reaction is the addition of hydrogen iodide to the double bond of styrene or acenaphthylene. The iodinated derivative formed in this manner gives a molecular compound with one molecule of iodine, which is the active center for the polymerization.

On the basis of the available data concerning the reaction mechanism, we have accepted the hypothesis of SAKURADA *et al.* This assumption is supported by our experimental results proving the ionic character of the reaction, the existence and perhaps the dissociation into ions of a molecular compound

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formed from acenaphthylene and iodine. On the other hand we believe that the oligomerization cannot proceed by a repeated cleavage and reformation of the covalent carbon iodine bond even if the latter is strongly polarized and weak.

Finally, the analytical results on the iodine content of the product are also inconsistent with the above conception. For reproducing the results reported in the above communications, we have investigated the kinetics of the iodine-induced oligomerization of acenaphthylene in dichloroethane as solvent.



Fig. 4. Conversion vs. time curves for oligomerization in dichloroethane at 30 and 0 °C Monomer concentration: 0.5 mol/l Iodine concentration: 0.015 mol/l

The conversion vs. time curves for the reactions carried out at 30 and 0 °C (Fig. 4) are similar to those reported in [5, 6] but 100% conversion is reached within about half the time. It seems likely that this is due to the more efficient drying in the present work. The decrease of temperature does not change the character of the curve and the rate is only slightly diminished. The latter fact supports the ionic mechanism of the reaction and contradicts the assumption of GIUSTI *et al.* 

Generally the rate of reaction proceeding by an ionic mechanism is strongly influenced by the dielectric constant of the medium. For this reason, the application of dichloroethane as a solvent with a relatively high dielectric constant\* (10.65 at 20 °C and 10.36 at 25 °C) is probably favourable for the oligomerization. Since such a positive effect of the reaction medium cannot

\* The used values of dielectric constants are from the U.S. Nat. Bureau of Standards, Circular No. 514.

be expected in the case of a solid state reaction, for better comparison, the process had to be studied also in a solvent with a low dielectric constant. For this purpose *n*-heptane has been chosen (dielectric constant 1.925 at 20 °C and 1.926 at 25 °C). In Fig. 5 are shown the conversion *vs.* time curves for the oligomerization in *n*-heptane at 30 and 0 °C. The character of the curves does not change relative to the previous ones but the rate of the process has decreased by about two orders of magnitude. Although the molecular decomposition assumed in [5, 6] may also be influenced by the dielectric constant of the medium, this fact again points to an ionic mechanism.



Fig. 5. Conversion vs. time curves for oligomerization in n-heptane at 30 and 0 °C Monomer concentration: 0.5 mol/l Iodine concentration: 0.015 mol/l

However, the reaction rates measured in the liquid and solid phase are now closer to each other.

The molecular weights of the oligomers obtained in the liquid state reaction are listed in Table III. The degrees of polymerization are between 5-13.

Significant dependences on conversion and time could not be established. It is noteworthy that GIUSTI *et al.* have reported much higher values (14—140), while the values (18—32) reported in their latter publication are only slightly higher than ours. On comparing the solid and liquid phase reactions, the following can be established:

(1) The rates of the liquid and solid phase reactions are quite different. This is understandable since the rate is greatly influenced by the dielectric constant of the medium. Also the probability of the favourable molecular collisions obviously depends on entirely different factors in the liquid than in the solid state.

(2) The conversion of the liquid phase reaction reaches 100%, whereas much lower conversion limits are observed in the solid state. This is in line with the expectations because in the liquid phase the reaction may go to completion without any hindrance but even in ideal crystals the structure of the lattice itself constitutes a barrier and the lattice defects and dislocations may play a similar role.

(3) The thermal behaviour and the molecular weight of the products formed in the two different phases are similar to each other.

On these grounds, it seems obvious that there is no possible way to draw a parallel between chain propagation and termination, but presumably, the processes have the same fundamentally ionic character and the initiation step may be the same.

#### **Table III**

Molecular weights of products obtained in iodine initiated liquid state oligomerization of acenaphthylene at different temperatures and conversions

Solvent	Temp. (°C)	Conversion	Mol. weight $\widetilde{M}_n$	Deg. pol. $\overline{P_n}$
Dichloroethane	30	12.2	790	5.2
		15.0	1040	6.8
		58.0	920	6.0
		92.3	870	5.7
		101.2	1130	7.4
Dichloroethane	0	16.5	1710	11.2
		56.2	1630	10.7
		82.7	2030	13.4
		99.2	1520	10.0
		102.0	1380	9.1
n-Heptane	30	8.6	650	4.2
		16.2	600	4.0
		23.2	680	4.5
		24.1	670	4.4
		27.4	680	4.5
		33.4	600	4.0
1-Heptane	0	19.3	720	4.7
		21.4	680	4.5
		25.9	830	5.5
		29.5	820	5.4
		33.2	770	5.0

Further evidence for the ionic character of this solid phase reaction is provided by the results obtained in the presence of water vapour. Water is known to be an effective inhibitor of ionic polymerization but has no influence on radical polymerization. Therefore, we have been investigating how this particular solid state oligomerization is influenced by the presence of water in







Fig. 7. Conversion vs. time curves for the solid state oligomerization of acenaphthylene at 60 °C. (1) Normal conditions, (2) with introduction of water vapour at the time indicated by the arrow

the system. It was established that no process occurred in samples where a layer of water had been placed under the crystalline acenaphthylene before starting the reaction. In the parallel samples containing no water the reaction took place in the usual way (Fig. 6). If water was added to the samples some time after starting the experiment, the amount of the oligomer obtained remained at the conversion value corresponding to the moment of the water addition (Fig. 7). This phenomenon cannot be due to the hindrance of iodine

adaption by water, *i.e.* displacement from the surface of the crystals by water, since iodine is adsorbed much stronger on the polar and hydrophobic acenaphthylene than water, and, besides, it forms a charge transfer complex with the solid.

The only possible explanation is chemical inhibition by water, which at the same time proves the ionic nature of the process. On the basis of the ionic mechanism of iodine initiated polymerizations reported thus far and of the comparison with the liquid state oligomerization of acenaphthylene, as well as of the results obtained on the effect of water vapour, the ionic character of solid state oligomerization can be considered as proved.

In connection with the nature of the initiation reaction, we have examined whether the jodine content of the product corresponds to the value expected from coupling of one iodine atom to one monomer molecule in this step. The iodine contents of oligomers produced under different conditions are presented in Table IV. This shows that the values obtained for solid state reactions are well below 0.2 and those for the liquid phase processes are also considerably smaller than 1. On this basis one must either suppose that a considerable part of the oligomer molecules have lost their iodine content due to hydrogen iodide elimination, or reject the above hypothesis concerning the initiation step. The problem could be cleared up by determining the double bond content of the product but such attempts have failed because of the side reactions (oxidation, chain degradation) taking place during the analysis. In spite of this, we do not assume that the initiation step involves bonding of an iodine atom or ion to acenaphthylene. Iodine is known to be a strong electron acceptor which forms charge-transfer complexes with aromatic compounds [17-19]. Obviously, acenaphthylene may also act as a donor but no spectroscopic evidence could be obtained for this, owing to the very intense and rich spectrum of acenaphthylene in the 200-340 nm region. However, we have investigated the change of extinction at the 524 nm band of iodine in n-heptane upon increasing the concentration of acenaphthylene, while keeping that of the iodine constant. The results are shown in Fig. 8. The extinction increases, then reaches a constant value at an iodine to acenaphthylene ratio of about 3. This typical saturation curve can be explained by the coordination of iodine molecules to acenaphthylene, resulting in a loosening of their electron structure. However, at an acenaphthylene concentration of about  $2 \times 10^{-2}$  mol/l the extinction starts to decrease linearly. This phenomenon has not been investigated but is probably due to the dissociation of the charge transfer complex into ions. Ionic iodine does not absorb at this wavelength. It must be noted that for the saturated analogue of acenaphthylene, i.e. acenaphthene, the linear decrease of the extinction has not been observed (Fig. 9). The obvious reason for this is the higher ionization potential of acenaphthene. Thus, in our opinion the initiation step in the oligomerization, on the basis of the hypothesis





To	1.1	-	T	Ta
1.8	D	е	1.1	a

Iodine	content	of the	oligomers	obtained	in	iodine	initiated	solid	state
		olige	omerizatio	n of acer	ap	hthylen	e		

Phase	Temp. (°C)	Conv. (%)	Iodine content iodine atom/ molecule
Solid	40	4.5	0.12
		11.2	0.08
		12.1	0.17
		14.2	0.04
		17.8	0.04
Solid	50	11.0	0.13
		23.2	0.13
		39.7	0.11
		46.2	0.07
	1	48.8	0.08
Solid	60	12.5	0.08
		26.0	0.09
		41.3	0.13
		44.8	0.16
		45.3	0.12
		48.4	0.06
Solid	70	8.0	0.07
		21.8	0.11
		24.3	0.15
		28.3	0.15
		31.9	0.11

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#### **Table IVb**

Iodine content of the oligomers obtained in iodine initiated liquid state oligomerization of acenaphthylene

Phase	Solvent	Temp (°C)	Conv. (%)	Iodine content iodine atom/ molecule
Liquid	Dichloroethane	30	37.0	0.14
			58.0	0.12
			91.2	0.10
			101.2	0.12
			102.3	0.08
Liquid	Dichloroethane	0	7.2	0.46
			56.2	0.28
			82.7	0.23
			99.2	0.29
			102.0	0.16
			102.3	0.18
Liquid	n-Heptane	30	4.0	0.28
			6.3	0.27
			17.6	0.24
			22.2	0.22
			36.3	0.20
Liquid	n-Heptane	0	6.7	0.48
			9.5	0.58
			16.6	0.53
			22.9	0.48
			31.5	0.47

of SAKURADA et al., would be the formation of a charge transfer complex between iodine and acenaphthylene (which corresponds to the ion pair formation assumed by SAKURADA et al.), followed by dissociation into ions. The question, whether initiation is brought about only by the acenaphthylene cation or also by the charge transfer complex itself, cannot be answered at present on the basis of our experiments.

Finally, it should be mentioned that neither the removal of oxygen from the samples, nor the quality of the solvent used for recrystallizing acenaphthylene had any observable effect on the progress of solid state polymerization or on the properties of the product formed.

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### RECENSIONES

#### XIIIth International Conference on Coordination Chemistry

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The book contains the papers serving as basis of the plenary lectures at the XIIIth International Conference on Coordination Chemistry organized in Poland in September 1970.

It is impossible to report in detail within the scope of a book review the 13 summary papers involving without exception a broad material. Therefore, only the subject and the most important conclusions of the single papers will be summarized.

J. C. BAILAR, Jr. gives an account of the main trends of research in coordination chemistry in the United States of America. The most important results attained in the investigation of complex compounds of various types are briefly described, and the relevant literature is given. This extensive list of reference makes the paper particularly valuable.

G. R. CHOPPIN deals with problems associated with the structure and thermodynamics of lanthanide and actinide complexes. He reports on the results of research concerned with the determination of the coordination number of lanthanides and actinides in solution. Factors determining and affecting the thermodynamic parameters of complex formation in solution are discussed in detail. Metal complexes of the outer sphere type are also treated.

B. B. CUNNINGHAM presented a paper on the physico-chemical properties of actinide complexes. Relationships between the coordination chemical properties of these elements and their place in the periodic system are shown. The properties of the actinides and their complexes are compared with those of other f transition elements and their compounds.

R. F. FENSKE's topic is the molecular orbital theory of  $\pi$ -donor and  $\pi$ -acceptor complexes. Possibilities and limitations of the application of MO calculations in the investigation of compounds of this type are shown. The possible use of these methods for the interpretation of absorption and photoelectronic spectra is indicated. Of particular interest is the part of the paper discussing the force constants of carbonyl complexes.

V. GUTMANN discusses in his paper the relationship between coordinative and redox properties in solution. The relationship between the donicity of the solvent and the redox potential of the dissolved particles is shown. Orientative rules are given concerning the effect of complex formation on redox properties, and on the effect of redox properties of the system on complex formation.

B. JEZOWSKA-TRZEBIATOWSKA discusses the theory and importance of oxygen bridging. The paper summarizes the results obtained in long years of research by the author and her research team.

S. F. A. KETTLE discusses the interpretation of vibrational spectra of solids. His work deals with some of the more important new results obtained in the field of the infrared and Raman spectroscopy of crystalline substances, from which conclusions of more general validity are drawn.

R. S. NYHOLM's paper concerns the synthesis, structure and reactions of metal-olefin complexes. The nature of the metal-olefin bond is discussed, several reactions of olefin coordinated to transition metals are presented, and factors affecting these reactions are discussed. Within this group of compounds, a few intramolecular rearrangements of particular interest are shown.

R. G. PEARSON discusses rules suitable for the investigation of the mechanism of inorganic reactions.

L. SACCONI reports results obtained in the investigation of iron(II), cobalt(II) and nickel(II) complexes with coordination numbers five and six. The effect of the geometry of the complexes on the spin state is dealt with in detail. Factors determining the magnetic properties of the complexes are discussed, with special reference to the interpretation of anomalous magnetic behaviour.

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V. I. SPITSYN reports the most important results attained in the last decade in the field of coordination chemistry in the USSR. Results obtained in the investigation of platinum metals, rare-earth metals and actinides are particularly emphasized. Several heteropolyacid systems, the complexes of ligands of novel type, organometallic compounds, and methods of investigation used for the study of the various types of complexes are also discussed. The paper closes with a detailed list of references, comprising mainly publications showing the results of recent years.

I. TSUJIKAWA treats in his paper the absorption lines of complexes of the iron group, summarizing the most important results attained in the last decade in this field.

K. B. YATSIMIRSKII discusses the role of coordination in catalytic redox processes. The fundamental theories of the subject are presented. The mechanisms of some of the most important catalytic redox processes are discussed. Factors influencing catalytic activity are indicated.

As can be seen also from this brief review, all the papers deal with fundamental problems of coordination chemistry. The material of the papers, the new scientific results, as well as the systematic survey of experimental results all contribute in making this publication very useful for coordination chemists.

K. BURGER

#### M. J. S. DEWAR: MO Theory as a Practical Tool for Studying Chemical Reactivity and

### W. ENGLAND, L. S. SALMON and K. RUEDENBERG: Localized Molecular Orbitals: A Bridge between Chemical Intuition and Molecular Quantum Mechanics

# Topics in Current Chemistry, Vol. 23, Ed. A. Davison, M.J.S. Dewar, K. Hafner, E. Heilbronner, U. Hoffmann, K. Niedenzu, Kl. Schäfer, G. Witting, Springer Verlag, Berlin-Heidelberg-New York 1971, 123. pp.

In the first paper of the volume M. J. S. DEWAR gives a critical review of the *ab initio* SCF MO method and the different semiempirical all-valence methods from the point of view of their applicability to the calculation of intramolecular and intermolecular potential energy surfaces. He shows the shortcomings and disadvantages of these methods used to calculate potential surfaces, which play an important role first of all in the theory of chemical reactivity based on quantum chemical scattering theory. Then he demonstrates that the MINDO/2 method, if properly parametrized, is capable of providing heats of formation, force constants and molecular geometries in a good agreement with experiment.

The method gives also reasonably good results for barriers to rotation about C=C bonds, for the activation energies of conformational isomerization and Cope rearrangement reactions, for the structures and reactions of 7-norbornyl ions and radicals and some other organic reactions discussed also in the paper. DEWAR points out, in agreement with the experience of the reviewer, that the MINDO/2 method does not always give good geometries for molecules which contain atoms with lone pairs. The author suggests for such cases the more refined NDDO MO method, but this method has not yet been parametrized for this purpose.

The paper is very clearly written and an ample material of numerical results, both theoretical and experimental, illustrates the different applications of the MINDO/2 method established by DEWAR and his coworkers. The paper is highly recommendable for physical chemists and organic chemists.

In the second paper written by ENGLAND *et al.* the question of localized orbitals (LO's) is discussed. As is well known, a Slater determinant total wave function is invariant under any orthogonal transformation formed with the aid of the linear combination of its one-electron orbitals. The authors show that, besides the total energy, its one-electron, Coulomb and exchange parts, as well as the first order density matrix and the Fock operator are also invariant under such a transformation. They point out further that only the solutions of the canonical Hartree-Fock equations (when all off-diagonal Lagrange multipliers are put equal to zero) are related to experimental quantities *via* Koopman's theorem.

The paper gives as criterion of localization that the sum for all occupied orbitals of all Coulomb integrals containing the squares of the same orbital for both electrons (the sum of

#### RECENSIONES

"self energies" of all occupied MO's) should be a maximum. Further the localized MO's have to be chosen to be orthogonal to assure their transferability between different molecules. For orbitals fulfilling this criterion the appropriate equations are written down. Also a discussion of the relation between the localized orbitals and the canonical HF orbitals and of the symmetry properties of the LO's is given at the end of the theoretical part of the paper. It is regrettable that the paper does not contain the review of other localization criteria and their critical discussion.

The last two chapters of the paper provide a systematic description of the LO's in diatomic molecules and of the  $\pi$  MO's in aromatic hydrocarbons. In the latter case they give a clear discussion of the delocalization in systems based on LO's and they classify the obtained unique set (with the exception of benzene) of localized  $\pi$  orbitals as different, essentially two-, three-, and four-center LO's. One of the greatest merits of the paper is that it contains detailed contours for the LO's in diatomic molecules and for the localized  $\pi$  MO's in aromatic hydrocarbons in 30 excellent figures.

The paper is clearly presented though it may not be always very easily readable for non-quantum chemists. Therefore, it can be recommended first of all to quantum chemists and physical chemists with appropriate knowledge in quantum chemistry.

J. LADIK



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#### ACTA CHIMICA

ТОМ 75 - ВЫП. 1

#### Проблемы, возникающие при анализе системы H<sub>2</sub>O<sub>2</sub>—Tl(III) Новые индуцированные реакции

Л. Й. ЧАНИ, Ф. ЧЕХ, Ж. СИЛ и Ж. БЁТИ

Новые индуцированные реакции наблюдались при одно-эквивалентном окислении (с помощью сульфата церия (IV) и/или перманганата калия) и восстановлении (ионами железа(II)) системы H<sub>2</sub>O<sub>2</sub>—Tl(III). Приводятся характеристики и возможный механизм индуцированных реакций.

## Сравнение некоторых методов расчета кинетики реакции, основанных на данных термических кривых

Т. ФЛОРА

На основе дериватографических кривых с помощью методов Фриман—Карролла, Хоровиц—Метцгера и Киссинжера, используя различные скорости нагрева, были рассчитаны энергии активации и порядок реакции термического разложения никель(II)-гексаминхлорида, сополимера полистирола с дивинилбензолом и Трихлорфона. Результаты, полученные различными методами и для различных типов реакций, сравнивались и интерпретировались.

#### О комплексах никеля (II) с этилендиаминэм

Й. ЧАСАР

Были изучены видимые и ИК спектры, а также магнитные свойства следующих комплексов [Nien<sub>3</sub>] $X_{\pi}$  (n = 1, 2;  $X = Cl^-$ , Br<sup>-</sup>,  $I^-$ , S<sub>2</sub>O<sub>3</sub><sup>-2</sup>; [PtCl<sub>4</sub>]<sup>-2</sup>) и [Nien<sub>2</sub>] $Y_{\pi}$  (n = 1, 2;  $Y = Cl^-$ , Br<sup>-</sup>, All<sub>2</sub><sup>-</sup>, Cul<sub>2</sub><sup>-</sup>, HgI<sub>4</sub><sup>-2</sup>, Ag(CN)<sub>2</sub><sup>-</sup>, Zn(CN)<sub>4</sub><sup>-2</sup>, Cd(CN)<sub>4</sub><sup>-2</sup>. Экспериментальные данные обсуждаются на основе теории лигандного поля. Подробно обсуждается возможность обнаружения полос колебания  $\nu(NiN)$ ; в выше приводимых комплексах эта полоса находится в области 500–540 см<sup>-1</sup>.

## Вывод уравнения турбулентности Рейнольдса на основе принципа Дьярмати

#### дь. винце

Было показано, что, подобно уравнению вязкого потока Навьер—Стокса, на основе интегрального принципа Дьярмати для неравновесной термодинамики может быть выведено и уравнение турбулентного потока Рейнольдса. В ходе вывода, потенциал диссипации Лоренцта был обобщен в некоторой мере. Демонстрируется, что плотность Лагранжа, в принципе Дьярмати, может быть разъединена на две различные части, относящиеся к основному и флуктуирующему движениям, соответственно. Справедливость дополнительной теоремы Дьярмати демонстрируется в случае квази-линейных составляющих уравнений. Было доказано, что вариационный принцип может быть использован также и в данных случаях.

#### Сжимаемость водных растворов отдельных галогенов, I Хлориды щелочных металлов

#### л. ОНИТИУ и Д. АУСЛЭНДЕР

Были исследованы изменения в адиабатической сжимаемости водных растворов LiCl, NaCl и KCl в зависимости от концентрации и температуры. Адиабатическая сжимае-

мость была рассчитана по формуле  $\beta_{ad} = \frac{1}{sv^2}$ , где S – плотность и V – скорость распрост-

ранения ультразвука, определяемы экспериментально. На первых трех рисунках приводится изменение сжимаемости в зависимости от температуры для трех различных солей; сжимаемость обычно уменьшается с увеличением температуры, достигает минимума, а затем изменяется в обратном направлении. С увеличением концентрации минимумы сдвигаются в направлении низких температур. На следующих трех рисунках приводится адиабатическая сжимаемость в зависимости от концентрации при постоянной температуре. В случае всех трех солей  $\beta_{ad}$  уменьшается с увеличением концентрации. Как вытекает из различных кривых, относящихся к различным температурам, с увеличением концентрации уменьшается влияние тепла на сжимаемость. Из следующего же рисунка видно, что в различных растворах солей  $\beta_{ad}$  обладает обратным изменением с диаметром катионов.

Изменение сжимаемости, в зависимости от температуры, концентрации растворов и диаметра катионов, отображает движение системы в сторону новых равновесий, а именно таких равновесий, которые определяются изменением связи между интенсивностями различных взаимодействий.

Далее обсуждается два известных, противоположных влияния повышения температуры на воду. При оценке результатов обсуждается влияние ионов на водородные связи, а также рассматриваются эффекты электросжатия. Адиабатическая сжимаемость, изменяющаяся в зависимости от катиона, объясняется с точки зрения представлений гидратационных сфер ионов.

#### Об электростатических теориях образования смешанных комплексов

#### Ф. ГАЙЗЕР и М. БЕК

Обсуждаются электростатические теории Кида и Маркуса—Элизера, объясняющие образование смешанных комплексов. Указывается, что теория Кида опирается лишь на атомные радиусы и не учитывает другие факторы. Основываясь на расчетах для смешанных комплексов HgBrI и FeFCl<sup>+</sup>, а также используя литературные данные — помимо прочего — было установлено, что электростатическая энергия стабилизации, рассчитанная по модели Маркуса—Элизера, составляет всего десять тысячных от энергии всех взаимодействий. Надежность этой, и без того малой величины, еще уменьшается с возможным изменением различных факторов (напр. длина связи, угол связи и пр.). Согласно моделям, энергии, рассчитанные для отдельных комплексов, даже качественно не согласуются с измеренными константами равновесия; и помимо этого обосновано существование  $HgF_2$  в водных растворах. Используя литературные данные, подчеркиваются трудности, возникающие при расчете диэлектрической постоянной растворителя.

#### Новые пути получения полиметилениминов

#### И. БЕК, Й. РАКОЦИ и Я. ТЁРЁК

Были исследованы возможности нового, экономичного синтеза циклоиминов с повышенным числом членов цикла (7, 8, 9), исходя из соответствующих лактамов. Приводится общая картина введенных изменений. В качестве модельного соединения был избран октагидроазоцин (гептаметиленимин), важный с точки зрения промышленности лекарственных веществ. Для него предлагается новый экономичный метод получения, осуществимый и в промышленном масштабе, и заключающийся в восстановлении О-метилового эфира энантолактима с помощью NaBH<sub>4</sub> в водных средах, содержащих органические кислоты в качестве буферов. Изучались также возможности приготовления и гидрирования бис-лактиминовых эфиров.

### Исследования в области твердофазной полимеризации, XXVIII Исследование твердофазной олигомеризации аценафтилена, инициированной йодом. Кинетика и механизм реакции

#### ДЬ. ХАРДИ, Г. КОВАЧ, ДЬ. КОСТЕРСИТЦ и Ф. ЧЕР

Были исследованы кинетика, механизм и условия олигомеризации кристалличе-ского аценафтилена, иницированной парами йода. Энергия активации брутто процесса, носящего линейный кинетический характер, равна 28 ккал/моль. Средняя степень полимеризации продуктов равна 3—6; содержание йода намного меньше одного атома на одну молекулу олигомера. Механизм реакции носит ионный характер. Вполне вероятно, что в качестве элементарной реакции инициирования может служить диссоциация на ионы КПЗ между йодом и аценафтиленом.



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#### by K. BURGER

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# GASCHROMATOGRAPHISCHE ANALYSE VON STICKOXIDEN, II

# ANALYSE VON NO2 MITTELS REAKTIONS-GASCHROMATOGRAPHIE

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Die Reaktion von NO<sub>2</sub> mit verschiedenen phosphororganischen Verbindungen, insbesondere Phosphinen und Phosphiten, wird auf ihre Eignung zur reaktions-gaschromatographischen Analyse des NO<sub>2</sub> geprüft. Es wird gefunden, daß die Reaktion mit Triphenylphosphit stöchiometrisch unter Bildung von NO verläuft. Die Reaktionsbedingungen und die Anwendung der Reaktion zur Analyse im Gemisch mit verschiedenen Bestandteilen werden beschrieben.

## Einleitung und Aufgabenstellung

Die bei der gaschromatographischen Analyse von Stickoxiden, insbesondere  $NO_2$ ,\* auftretenden Schwierigkeiten haben verschiedene Autoren veranlaßt, reaktions-gaschromatographische Verfahren heranzuziehen. Dabei wird durch eine geeignete chemische Reaktion, die auf einer der Trennsäule vorgeschalteten Säule abläuft, das  $NO_2$  in eine leichter zu handhabende Verbindung überführt und diese gaschromatographisch bestimmt. GREENE und PUST [1] verwendeten die Reaktion

$$3N_2O_4 + 2H_2O = 2NO + 4HNO_3$$
(1)

wozu eine 3 m lange, mit nichtaktiviertem Molekularsieb 5A gefüllte Trennsäule mit 2 ml H<sub>2</sub>O beladen wurde. Zur Anwendung dieses Verfahrens auf  $O_2$ -haltige Gasgemische kondensieren SMITH u. Mitarb. [2] zunächst das NO<sub>2</sub> vor der Trennsäule und eluieren die Begleitgase, bevor NO<sub>2</sub> verdampft und nach Gl. (1) umgesetzt wird.

MIKKELSEN und Mitarb. [3] benutzten die Reaktion

$$\frac{3NO_2 + Na_2B_4O_7 \cdot 10H_2O = 2NaNO_3 + 2B_2O_3 + 10H_2O + NO.}{(2)}$$

Die Reaktionssäule enthielt ein Gemisch von Borax und Chromosorb und war einer Molekularsieb 5A-Säule vorgeschaltet. MURACA u. Mitarb. [4] beschreiben

\* Unter NO<sub>2</sub> wird, sofern nicht anders vermerkt, das Gleichgewichtsgemisch N<sub>2</sub>O<sub>4</sub>  $\rightleftharpoons$  2NO<sub>2</sub> verstanden.

die Überführung von  $N_2O_4$  und anderer Stickoxide in  $N_2$  an Cu-Pulver bei 800 °C nach Art des Dumas-Verfahrens mit nachfolgender Analyse der gebildeten Inertgase an einer Porapak-Säule.

KEKEH [5] benutzte als Reaktionsschicht Cu-Pulver, das auf Chromosorb P aufgetragen war. Die Reduktion des NO<sub>2</sub> zu NO erfolgte bei 45°.

Die Zahl der Reaktionen, die zur reaktions-gaschromatographischen Bestimmung des  $NO_2$  geeignet sind, ist offenbar recht begrenzt. Ein Grund hierfür liegt darin, daß trotz der großen Reaktivität des  $NO_2$  nur wenige seiner Reaktionen stöchiometrisch einheitlich verlaufen. Damit wird ihre analytische Anwendbarkeit erschwert bzw. unmöglich gemacht.

Die bisher beschriebenen reaktions-gaschromatographischen Verfahren weisen den Mangel auf, daß ihre Durchführung die Analyse des  $NO_2$  nur in Gemischen zuläßt, die vorwiegend aus Inertgasen bestehen. Weiterhin zeigen die Gleichungen (1) und (2), daß die Stöchiometrie dieser Reaktionen für reaktions-gaschromatographische Untersuchungen nicht optimal ist, da zwei N-haltige Reaktionsprodukte entstehen, jedoch nur NO in den Detektor gelangt. Ziel der vorliegenden Arbeit war es, eine geeignete Reaktion aufzufinden, die diesen Einschränkungen nicht unterliegt.

# Die Reaktionen von Stickoxiden mit phosphororganischen Verbindungen

Für analytische Untersuchungen mittels Reaktions-Gaschromatographie ist es zweifellos vorteilhaft, wenn man katalytische Umwandlungen heranziehen kann. Jedoch treten bei Einhaltung der erforderlichen Reaktionsbedingungen oftmals Komplikationen durch die übrigen Gemischbestandteile ein, entweder in Form unerwünschter Nebenreaktionen oder durch Vergiftungserscheinungen am Katalysator. Man kann dann nur auf stöchiometrisch ablaufende Reaktionen zurückgreifen und muß versuchen, die Nachteile, die sich aus der fortschreitenden Erschöpfung der Reaktionssäule ergeben, durch optimale Wahl der Analysenbedingungen möglichst gering zu halten.

Bei der Suche nach geeigneten Reaktionspartnern wurde das Verhalten verschiedener Organophosphorverbindungen gegenüber Stickoxiden geprüft.

Trisubstituierte Phosphine  $R_3P$  und Phosphite  $(RO)_3P$  (R = Alkyl, Aryl) besitzen auf Grund des freien Elektronenpaares am P-Atom eine ausgeprägte nucleophile Reaktivität. Sie reagieren mit zahlreichen O-haltigen Verbindungen wie Hydroperoxiden, Ozon, Aminoxiden, Epoxiden, Stickoxiden, zumeist unter Bildung der entsprechenden Phosphinoxide bzw. Phosphate.

Übersichten über diese Reaktionen geben CADOGAN [6], HUDSON [7] sowie KIRBY und WARREN [8]. Zum Teil haben diese Reaktionen analytische Anwendungen gefunden [9, 10].

Bei geeigneter Wahl der Substituenten liegen phosphororganische Verbindungen als Flüssigkeiten hinreichend geringer Flüchtigkeit vor. Die Umset-

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zung mit Stickoxiden sind Reaktionen des Typs

$$A_{fl.} + B_{gas} \rightarrow C_{fl. oder fest} + D_{gas}.$$
 (3)

Die Reaktionsprodukte C, Phosphate bzw. Phosphinoxide, sind von noch geringerer Flüchtigkeit und verbleiben in der Reaktionssäule. In den Detektor gelangen lediglich die gasförmigen Reaktionsprodukte. Damit erfüllen die genannten Organophosphorverbindungen wichtige Voraussetzungen für ihre Anwendung unter reaktions-gaschromatographischen Bedingungen.

Als Reaktionsprodukte der Umsetzung von  $NO_2$  mit Phosphiten, Phosphinen, Pyrophosphiten treten NO,  $N_2O$  sowie  $N_2$  in unterschiedlichen Verhältnissen auf [7, 10, 11].

Für die Gewährleistung eines Reaktionsverlaufes, der zu einem einheitlichen Reaktionsprodukt führt, ist von Bedeutung, daß auch NO mit einer Anzahl P-organischer Verbindungen reagieren kann [12, 13]:

$$(OR)_{3}P + 2NO \rightarrow (OR)_{3}PO + N_{2}O.$$
(4)

Nach DRAGO [14] sind solche Reaktionen nur möglich, wenn die P-Verbindung eine zur Reaktion mit der schwachen Lewis-Säure NO ausreichende Basizität besitzt.



Abb. 1. Gasförmige Reaktionsprodukte der Umsetzung von Tri-n-butylphosphit mit NO<sub>2</sub>. Reaktionssäule:  $150 \times 0.5$  cm, 30 Gew.%  $(n-C_4H_9O)_3P$  auf Sterchamol (0,3-0.5 mm). Trennsäulen:  $1: 50 \times 0.5$  cm, Silibor (20),  $2: 200 \times 0.5$  cm, Molekularsieb 5 A. Trägergas: Elektrolyt/ wasserstoff, 3.6 l/h. Detektor: Wärmeleitfähigkeitszelle

In Gl. (4) ist dies für R = Alkyl (+I-Effekt) der Fall, für R = Aryl (-I-Effekt) dagegen nicht. Nimmt man an, daß bei der Reaktion mit  $NO_2$  zunächst NO gebildet wird, so erhält man ein einheitliches Reaktionsprodukt, wenn eine P-Verbindung mit geringer Basizität als Reaktionspartner gewählt wird, bei der die Reduktion des  $NO_2$  auf der NO-Stufe stehen bleibt. Bei der Kombination von Reaktionssäulen  $(50 \times 0.5 \text{ cm})$ , die als reaktive Phase 20-30 Gew.-% Tri-*n*-butylphosphit, Tri-*n*-octylphosphit, Triphenylphosphin, Hexamethylphosphorigsäureamid sowie Triphenylphosphit auf Sterchamol als Trägermaterial enthielten, mit geeigneten Trennsäulen wurden bei vollständigem Umsatz von  $NO_2$  als Reaktionsprodukte  $NO, N_2O$  und  $N_2$  in wechselnden Verhältnissen gefunden. Abb. 1 zeigt die im Falle des Tri-*n*-butylphosphits

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gefundenen Verhältnisse. Hexamethylphosphorigsäureamid besitzt die größte Basizität der untersuchten Verbindungen. Die gasförmigen Bestandteile bestehen in diesem Falle zu 94% aus N<sub>2</sub>O und zu 6% aus N<sub>2</sub>. Abb. 2 zeigt, daß die Reaktionsprodukte hier unabhängig von der Probengröße in konstantem Verhältnis gebildet werden. Im Falle des Triphenylphosphins reicht die



Abb. 2. Gasförmige Reaktionsprodukte der Umsetzung von Hexaäthylphosphorigsäureamid mit NO<sub>2</sub> in Abhängigkeit von Probevolumen. Reaktionssäule:  $50 \times 0.5$  cm, 30 Gew.% [N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>P auf Sterchamol (0,3-0,5 mm). Trennsäule:  $200 \times 0.5$  cm, Silibor (20). Trägergas: Elektrolytwasserstoff, 3,6 l/h. Detektor: Wärmeleitfähigkeitszelle



Abb. 3. Gasförmige Reaktionsprodukte der Umsetzung von Triphenylphosphin mit NO<sub>2</sub>. Reaktionssäule:  $50 \times 0.5$  cm, 20 Gew.% (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>P auf Sterchamol, 100 °C. Trennsälen: 1:  $200 \times 0.5$  cm, Silibor (20). 2:  $150 \times 0.5$  cm, Molekularsieb 5 A. Trägergas: Elektrolytwasserstoff, 3,6 l/h. Detektor: Wärmeleitfähigkeitszelle

Basizität noch aus, um eine Reaktion mit NO zu gewährleisten. Erwartungsgemäß erhält man kein einheitliches Reaktionsprodukt (Abb. 3). Die Untersuchung der Reaktion des Triphenylphosphins mit NO ergab ein zu 80% aus  $N_2O$  und zu 20% aus  $N_2$  bestehendes Gasgemisch [15].

Demgegenüber reicht die Basizität des Triphenylphosphits für die Reaktion mit NO nicht aus. Man kann daher mit  $NO_2$  als Reaktionspartner einen Reaktionsverlauf nach der Gleichung

$$(C_6H_5O)_3P + NO_2 = (C_6H_5O)_3PO + NO$$
 (5)

erwarten.

# Die Reaktion von NO<sub>2</sub> mit Triphenylphosphit

Zur Untersuchung der Stöchiometrie der Reaktion unter den Bedingungen der Reaktions-Gaschromatographie war die Einhaltung konstanter Arbeitsbedingungen erforderlich. Insbesondere mußte die Temperatur konstant gehalten werden, um das Gleichgewicht  $N_2O_4 \rightleftharpoons 2NO_2$  zu berücksichtigen.  $NO_2$ -Vorratsgefäß, Dosiersystem und Reaktionssäule wurden auf 27,0° ± 0,1 °C gehalten. Bei dieser Temperatur beträgt der Dissoziationsgrad des  $N_2O_4$ 20,0% [16].

Weiterhin mußte der Ausschluß von Feuchtigkeit aus dem Reaktionssystem gewährleistet sein, da mit Wasser eine Nebenreaktion eintreten kann. Im Reaktionsprodukt tritt dann N<sub>2</sub> auf. Eine Erklärung hierfür kann darin liegen, daß durch Hydrolyse von Triphenylphosphit gebildetes Diphenylphosphonat mit NO unter N<sub>2</sub>-Bildung reagieren kann [17]. Für alle Versuche wurde ausschließlich frisch destilliertes Triphenylphosphit eingesetzt. Das Aufbringen auf das Trägermaterial erfolgte mit wasserfreiem Äther, die verwendeten Gase wurden ebenfalls getrocknet. Über die Geschwindigkeit der Reaktion von NO<sub>2</sub> mit P-organischen Verbindungen liegen keine Angaben vor. Sie verläuft offensichtlich sehr schnell, denn auch bei kurzen Verweilzeiten auf der Reaktionssäule (10 cm Säulenlänge, Trägergasgeschwindigkeit 10 l H<sub>2</sub>/h) konnte auf einer nachgeschalteten Trennsäule mit Heydeflon (Teflon) als stationärer Phase kein NO<sub>2</sub> mehr nachgewiesen werden [20]. An derselben Trennsäule wurde auf Abwesenheit von N<sub>2</sub>O geprüft. Das gebildete NO wurde auf einer Säule mit Molekularsieb 5A qualitativ und quantitativ bestimmt.

Zur Untersuchung der Stöchiometrie der Reaktion wurden die bei der Dosierung gleicher Probevolumina NO und  $NO_2$  erhaltenen Peakflächen bestimmt und unter Berücksichtigung des Anteils, der als  $N_2O_4$  vorliegt, in Beziehung gesetzt. Abb. 4 und Tab. I zeigen, daß zwischen den bei der Umwandlung von  $NO_2$  zu NO experimentell gefundenen und den rechnerisch erhaltenen Peakflächen befriedigende Übereinstimmung besteht. Wiederholung der Versuche unter Variation der Beladung der Reaktionssäule mit



Abb. 4. Zur Stöchiometrie der Umsetzung von Triphenylphosphit mit NO<sub>2</sub>. Kurve I: Abhängigkeit der Peakfläche vom Probevolumen bei Dosierung von NO. Kurve II: Abhängigkeit der Peakfläche vom Probevolumen bei Dosierung von NO<sub>2</sub> und Umwandlung auf der Reaktionssäule zu NO (27 °C).  $\odot$  gefundene Werte,  $\times$  berechnete Werte ( $\alpha_{N_2O_4} = 0,20$ )

Triphenylphosphit zwischen 20 und 40 Gew. %, der Art des Trägermaterials (Sterchamol, Teflex, Heydeflon), der Länge der nachgeschalteten Molekularsieb 5A-Trennsäule (0,5–2 m), der Art (H<sub>2</sub>, Ar) und der Geschwindigkeit des Trägergases ergaben Übereinstimmung.

# **Tabelle** I

Probe- volumen NO <sub>2</sub>	Peakfläche NO, cm <sup>2</sup>		⊿, %
ml	ber.	gef.	
0,2	22,6	22,3	-1,3
0,5	53,5	51,3	-4,1
0,7	74,2	74,0	-0,3
0,8	84,6	84,9	+0,4
1,0	105,6	106,1	+0,5
1,2	126,0	124,3	-1,4

Zur Stöchiometrie der Reaktion  $(C_6H_5O)_3P + NO_2 \rightarrow (C_6H_5O)_3PO + NO_2$ 

Man kann somit feststellen, daß die Reaktion nach Gl. (5), oder unter Berücksichtigung von  $N_2O_4$  als Reaktionspartner

$$2(C_6H_5O)_3P + N_2O_4 = 2(C_6H_5O)_3PO + 2NO$$
(6)

zur reaktions-gaschromatographischen Analyse von  $NO_2$  herangezogen werden kann. Der Vorteil der Stöchiometrie der Reaktionen (5) bzw. (6) gegenüber



Abb. 5. Analyse eines NO<sub>2</sub>-haltigen Gasgemisches mittels Reaktions-Gaschromatographie. Reaktionssäule:  $50 \times 0.5$  cm, 20 Gew. $_{0}^{\circ}$  (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>P auf Sterchamol (0,3-0,5 mm), 27 °C. Trennsäule:  $200 \times 0.5$  cm, Molekularsieb 5 A, 70 °C. Trägergas: Elektrolytwasserstoff, 3,6 l/h. Detektor: Wärmeleitfähigkeitszelle



Abb. 6. Analyse eines Gemisches aus NO<sub>2</sub> und gesättigten Kohlenwasserstoffen mittels Reaktions-Gaschromatographie. Reaktionssäule: vgl. Abb. 5. Trennsäule: 200×0,5 cm, Porapak Q, 100 °C. Trägergas: Elektrolytwasserstoff, 3,6 l/h. Detektor: Wärmeleitfähigkeitszelle

Reaktion (1) und (2) ist augenfällig. Die Flüchtigkeit des Triphenylphosphits läßt Arbeitstemperaturen bis 70 °C zu. Nachdem sich so die prinzipielle Eignung des Triphenylphosphits zur reaktions-gaschromatographischen Bestimmung des  $NO_2$  erwiesen hatte, wurden verschiedene Gasgemische, die  $NO_2$ enthielten, mit dieser Methode untersucht. Abb. 5 und 6 zeigen Beispiele hierfür.

In Tab. II sind die Ergebnisse quantitativer Analysen eines  $NO_2$ -Ar-Gemisches (50,0:50,0) in Abhängigkeit vom dosierten Probevolumen zusam-

Тя	h	el	le	I	τ
		0.	a.c.		

Analyse eines NO<sub>2</sub>-Ar-Gemisches (50:50) in Abhängigkeit on der Probengröße Reaktionssäule:  $50 \times 0.5$  cm. 20 Gew.% ( $C_6H_5O$ )<sub>3</sub>P auf Heydeflon, 27 °C Trägergas:  $H_2$  (3.6 l/h)

0,247 0,375	${ m NO}_2$ , gefunden Vol%
0,247	52,5
	52,5
	51,0
0,375	47,5
	49,2
	49,2
0,461	49,2
	52,7
0,527	50,8
	50,6
0,764	50,7
	51,7
	53,0

mengestellt. Das Gasgemisch wurde für jedes Probevolumen neu hergestellt. Die quantitative Auswertung erfolgte über eine mit reinem NO<sub>2</sub> aufgenommene Eichkurve. Als Meßgrößen dienten die Peakflächen. Die statistische Auswertung ergab einen Mittelwert von  $(50.8 \pm 1.0)$  % NO<sub>2</sub> bei einer statistischen Sicherheit von P = 95% und f = 12 Freiheitsgraden. Die Prüfung mit Hilfe des t-Testes zeigt, daß der zwischen wahrem Wert und experimentell gefundenem Mittelwert gefundene Unterschied durch Zufallsfehler bedingt ist [18]. In Tab. III sind Ergebnisse zusammengefaßt, die bei der Anwendung der Methode auf weitere Gasgemische erhalten wurden. Die erhaltenen Standardabweichungen (bei P = 95%) liegen zwischen 3 und 6% relativ. Anwendung des t-Testes zeigt auch hier, daß die Unterschiede zwischen den wahren Werten und den Mittelwerten durch Zufallsfehler bedingt sind.

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#### Tabelle III

Analyse NO<sub>3</sub>-haltiger Gasgemische.

Reaktionssäule: 50 cm×5 mm, 30% Gew.% (CsH50)3P. Trennsäule: 2 m. Molekularsieb 5A

Nr.	Gemischbestandteil	$NO_2$ , $Vol_0$	n	$x + \Delta \bar{x} (P = 95\%)$	S rel (%)
1	Ar	50,0	13	$50,8\pm1,0$	3,35
2	Ar	30,0	14	$29,3\pm1,0$	5,99
3	Ar	35,0	17	$35,9\pm0,6$	2,99
4	$H_2$	50,0	31	$51,7\pm0,7$	3,42
5	$\mathbf{N}_{2}$	65,0	7	$66,3\pm2,5$	4,09
6	$O_2, N_2$	35,0	4	$36,6\pm2,3$	4,25
7	$CO, N_2$	45,0	5	$46,7\pm3,6$	6,43
	, 2			, <u> </u>	

 $\overline{x} = Mittelwert$ 

n =Zahl der Parallelbestimmungen

 $\Delta \bar{x} = \text{Vertrauensintervall von } \bar{x}$ 

S = relative Standardabweichung

Zur Analyse des Gemisches Nr. 6 in Tab. III wurde NO2 ähnlich wie bei SMITH u. a. [2] zunächst durch Auskondensieren aus der Probe abgetrennt und danach umgesetzt und analysiert. Der Analysenfehler ist nur wenig größer als bei den anderen Beispielen.

Liegen in der Analysenprobe NO und NO, gemeinsam vor, so erhält man einen gemeinsamen Peak. Zur getrennten Erfassung kann man wie im vorangehenden Beispiel wiederum durch Ausfrieren zunächst das NO, abtrennen. Für NO- und NO2-haltige Gasgemische hat TROWELL [19] eine derartige Arbeitsweise beschrieben. Die quantitative Analyse derartiger Gemische wurde in Rahmen dieser Arbeit nicht untersucht.

# Experimentelles

Die verwendete gaschromatographische Apparatur, die Herstellung des Stickoxide, die Herkunft der verwendeten Trägermaterialien, die zur Analyse der Stickoxide verwendeten

die Herkunft der verwendeten Trägermaterialien, die zur Analyse der Stickoxide verwendeten Trennsäulen wurden bereits beschrieben [20].
Die verwendeten P-organischen Verbindungen hatten folgende Charakteristika: Triphenylphosphit (VEB Chemiewerk Greiz—Dölau) Kp<sup>1</sup>182—186 °C, nD<sup>25</sup> 1,5893, Lit. 1,5850 [21]. Tributylphosphit (FERAK, Berlin) Kp<sup>0,1</sup> 87—92 °C, nD<sup>20</sup> = 1,4320, Lit. 1,4320 [22].
Triphenylphosphin (FERAK, Berlin), F 80,5 °C, Lit. 79,5 °C [23]. Hexaäthylphosphorigsöureamid nach der Methode von STUEBE und LANKELMA [24], Kp<sup>0,1</sup> = 85—90 °C, nD<sup>20</sup> = 1,4736, Lit. 1,4758 [24]. Tri-n-octylphosphit [22], Kp<sup>0,1</sup> = 178 — 183 °C.

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# NH STRETCHING VIBRATION BANDS AT WAVENUMBERS LOWER THAN 3000 cm<sup>-1</sup>, VIII

CYCLIC DIMERIC STRUCTURES THIAZOLINE AND THIAZINE DERIVATIVES

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It is proved by IR spectroscopy that N-arylthioureas react with  $\alpha, \omega$ -dihaloalkanes to give compounds of structure II. The IR spectra of these compounds are significantly different from that of the corresponding thiazolines and thiazines (I). The deviations in the spectra of the latter two types make the two tautomeric structures Ia and Ib probable. The association structures formed by these three types of compounds in the solid state are also different.

N-Aryl- (or aralkyl-), N' $\beta$ - (or  $\gamma$ -)hydroxyalkylthioureas give in a ring closure reaction [1-3] 2-arylaminothiazolines (I, n = 2) and the analogous thiazines (I, n = 3), respectively. Compounds of structure I can exist in the two tautomeric forms Ia and Ib. N-Aryl-(or aralkyl-)-thioureas yield with 1,3dihaloalkanes according to the literature [1] the same derivative of structure I and alkylene-bis-thiuronium salts [4, 5] as by-products. In a reexamination of



this latter method we have shown [6], that no compounds corresponding to structure I were formed. According to this reaction two other structures (II and III) should be taken into consideration, and the latter in two possible tautomeric forms, IIIa and IIIb. We could show, that in all investigated cases (with 1,2-dihaloalkanes, too) compounds of structure II were formed, which sometimes contained some of the thiuronium salt as a by-product [7]. Struc-



IIIa

IIIb

ture I could be ruled out, as the corresponding compounds were not identical with the authentic derivatives of I, which had been synthesized by unambiguous routes [1-3]. Structure III was excluded on the evidence of the IR spectra.

It seemed to be worthwhile to investigate the influence of the molecular structure (the character of the aryl substituent, the size of the hetero ring, etc.) upon the tautomeric equilibrium of the compounds with structure I. For this purpose — as well as for the structure determinaton — spectroscopic methods seem to be the most suitable.

In the literature only few data can be found about the spectroscopic investigation of compounds analogous to the tautomers Ia and Ib. These data [3, 8-16], in spite of including UV, IR and NMR investigations, did not prove unambiguously the structure of the tautomers, as the different methods led to contradictions.

From our own IR investigations it became evident that the tautomers of compound I form mesomeric systems (Ia'  $\leftrightarrow$  Ia'', Ib'  $\leftrightarrow$  Ib''). In these systems the equilibrium may be shifted towards Ia' or Ia'' and Ib' or Ib'' respectively, depending on the size of the hetero ring, on the substituents, etc. As changes in the electron distribution of the mesomeric system may have a similar effect on the spectra as the shift of the tautomeric equilibrium, no derivative characterized unambiguously by structure Ia and Ib, respectively, could be detected, in spite of investigating a large number of model compounds. (*E.g.*, a shift of the Ib'  $\leftrightarrow$  Ib'' system towards the latter would cause a similar increase in the  $\nu$ C=N frequency and the  $\delta$ NCH<sub>2</sub> chemical shift as would Ib  $\rightarrow$  Ia tautomerization.)

The spectra of the compounds with structure I could be readily divided into two groups according to their different parameters, but these two groups were constituted by compounds differing in the size of the hetero ring, as the thiazolines belonged to one, and the thiazines to the other group. Therefore it was dubious, whether the different ring size causes only a change in the mesomeric systems, or the tautomerism is also influenced. The differences in the spectra may be due either to different tautomeric structures or to changes in the Ia' – Ia'' and Ib' – Ib'' mesomeric systems. That is, the size of the hetero ring will influence only the electron distribution within the mesomeric system, and the distribution of the double bond cannot be fixed. Nevertheless, supposing only changes in the electron distribution, the spectra indicated which of the extreme structures, Ia' or Ia" and Ib' or Ib", respectively, is predominant; on the other hand supposing only a shift in the tautomeric equilibrium, the structure valid for the thiazines (Ib) and thiazolines (Ia), respectively, can be established. We could show by other spectroscopic methods that thiazolines and thiazines differ in their tautomeric structures and these results are in agreement with the conclusions drawn from the IR spectra [17, 18].

In the case of the N-substituted (alkyl, acyl) derivatives, the isomers belonging to the tautomers Ia and Ib can be distinguished more easily [17-22].

The IR investigation of structures I was instructive first of all because it gave information on the associated structures formed in the solid phase.

The reaction of N-aryl- (or aralkyl-) thioureas with 1,2- or 1,3-dihaloalkanes led to compounds (II) with similar IR spectra, independently of the size of the hetero ring formed. On the other hand, the ring closure of N' $\beta$ - or  $\gamma$ -hydroxyalkyl-N-aryl- (or aralkyl-) thioureas yielded the isomers I which afforded two similar kinds of infrared spectra, which were different from that of the compounds II mentioned above.

Accordingly, the spectra of the investigated compounds can be divided into three ("A", "B" and "C") types (see Table I), differing mainly in the region of the NH stretching vibration ( $\nu$ NH) and of the double bonds between 1700 and 1500 cm<sup>-1</sup> — where the  $\nu$ C=N-type group-frequency appears.

In the spectra of type "A" of compounds II, the very sharp and weak  $\nu$ NH band (at about 3300 cm<sup>-1</sup>) is in some cases hardly significant and split (Fig. 1), or it is shifted towards the smaller wavenumbers by 10–20 cm<sup>-1</sup> and it is somewhat more intense and broader (Fig. 2). In the region of the double bond there is only one very intense and sharp maximum besides the aromatic skeletal vibration, at about 1600 cm<sup>-1</sup> (Figs 1-4).

In the spectra of compounds of structure I the  $\nu$ NH band is always very strong and is divided into two main maxima and several sub-maxima. The







Fig. 2. IR spectrum of II (Ar = 2,6-dimethylphenyl, n = 2)







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# Table I

The vNH and vC=N frequencies of compounds of types 1-4 (in cm<sup>-1</sup>)



3A





Struc- ture	Type of spec- trum	Ar	R1	R <sub>2</sub>	R <sub>3</sub>	PNH band	Group vibra- tion of type vC=N
1	С		Н	H		3300-2600	1655
3	Α	CH <sub>3</sub>	н	н	-	3270	1585
1	С	1	н	Me	-	3300 - 2600	1650
3	A	$\langle () \rangle$	Me	н	-	3240	1590
3	A		$\rm CH_2OH$	H		3270	1610
2	В	CH <sub>3</sub>	н	H	н	3250 - 2750	1625
4	Α		н	H	н	3305	1570
1	C		н	н	_	3300-2600	1645
3	A		н	н		3320	1600
1	C	Cl	н	Me	_	3300 - 2600	1645
3	A		Me	н	_	3340	1610
3	A	$\langle \bigcirc \rangle$ -	CH <sub>2</sub> OH	н		3270	1610
2	В	$\underline{\vee}$	н	н	н	3250 - 2800	1625
4	A	Cl	н	н	н	3300	1570
4	A		н	H	Me	3310	1575
4	A	and the second	Me	н	н	3305	1560
1	C	CH <sub>3</sub>	Н	н		3300-2600	1625
2	В	H <sub>3</sub> C-	н	н	н	3300- 2600	1640

Struc- ture	Type of spec- trum	Ar	R1	R <sub>2</sub>	$R_3$	vNH band	Group vibra- tion of type $\nu C=N$
1	C	1	н	н	_	3300-2600	1655
3	A	CH <sub>3</sub>	н	H	-	3235	1600
1	C	Br_	н	Me	_	3300-2600	1660 1645
3	A		CH <sub>2</sub> OH	н	-	3335	1605
2	В	CH <sub>3</sub>	н	н	H	3300-2600	1625
4	A		Η	H	H	3280	1555
1	С	CH <sub>3</sub>	н	н	_	3300-2600	1650
3	A	- 6	н	н	-	3240	1600
1	C	Br-()-	н	Me	_	3300-2600	1650
4	A	Br	н	н	н	3270	1570
1	C	CH	н	н	_	3300-2600	1650
3	A	C113	н	н	-	3315	1610
1	C	$\left( \right) $	Η	Me	-	3300-2600	1645
3	A		$\rm CH_2OH$	H	-	3330	1600
2	В	O.N CH.	Н	Н	H	3300 - 2600	1615
4	A	2 0	н	Н	Н	3285	1560
1	C	Ph	н	н	_	3300-2600	1640
1	C		н	Me	-	3300-2600	1650
2	В	Br	н	н	H	3300-2600	1630
1	C	CH <sub>3</sub>	н	н		3300-2600	1650
1	C	H <sub>3</sub> C-()-	н	Me	_	3300-2600	1640
2	В	Br CH <sub>3</sub>	н	н	н	3300-2600	1615
1	C	CH <sub>3</sub>	Ĥ	н	_	3300-2600	1645
1	C	Br O	н	Me	-	3300 - 2600	1650
3	A		$CH_2OH$	н	-	3340	1610
2	В	O <sub>2</sub> N CH <sub>3</sub>	Н	H	H	3300-2600	1630

Table I (continued)

Struc- ture	Type of spec- trum	Ar	R <sub>1</sub>	R <sub>2</sub>	$R_3$	vNH band	Group vibra- tion of type $\nu C=N$
1	С		Н	Me	-	3300-2600	1640
1	C		Н	Me	-	3300-2600	1645
1	С	F O O	н	Me	_	3300-2600	1650
1	C i		н	Me	-	3300-2600	1645

Table I (continued)

absorption of these two parts is found at 3300 - 3000 and 3000 - 2600 cm<sup>-1</sup>, respectively. The two types of spectra differ in the total intensity of the *v*NH band, in the intensity of the two main maxima and in the degree of their separation.

In the spectra of type "B" (Figs 5 and 6) of thiazines the two main maxima are not well divided; the maximum at higher wavenumbers is weaker and is often split into a doublet or a quartet. The  $\nu$ C=N band belonging to the cyclic thiourea group appears in the region of 1635 - 1625 cm<sup>-1</sup> and is very sharp.



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In the spectra of type "C" (Figs 7 and 8) of thiazolines the  $\nu$ NH band is a little more intense, and the relative intensity of the maximum at the higher wavenumbers increases, too. Consequently, these two maxima are almost equal and well separated. In the region of the double bond there appears a very intense and somewhat broadened maximum at 1650 cm<sup>-1</sup> having frequently a shoulder.

The data of the "A"-type spectra exclude the possibility of structure III. IIIb is not possible, as the  $\nu$ NH band has been detected in all spectra. Structure IIIa can be ruled out on account of the high intensity of the band in the region of the double bond. The spectra of thioamides have an absorption in the region 1650–1550 cm<sup>-1</sup> [23, 24] (thioamide-A band [23]), but this is — similarly to the amid-II band of lactams [25–27] — far weaker and broader,







especially in N-monosubstituted derivatives [28]. Further data excluding structure III are provided by the spectra of the acyl derivatives [21].

Thus to the compounds giving "A"-type spectra, structure II can be assigned, in which the imino hydrogen — partly owing to its more basic character and partly because of its more unfavoured steric position — does not take part in any association. Furthermore, as the molecules with structure II contain no electron donor atom, which would be required for the formation of hydrogen bridges — the imino group is monomeric state in most of the investigated compounds. This results in the appearance of an exceptionally weak, sharp  $\nu$ NH band, which is characteristic of this type of compounds. (The acyl derivatives further support structure II [21].)

The spectral data mentioned above are in good agreement with the spectra of types "B" and "C" of the isomers I. The C=N double bond should appear, as a result of conjugation, at lower frequencies in the tautomers Ib than in the tautomers Ia [26, 27]. As in the spectra of type "C" there is an absorption at about 1650 cm<sup>-1</sup> which appears in the "B"-type spectra between 1635-1626 cm<sup>-1</sup>, the former may correspond to structure Ia and latter to Ib. Nevertheless, it should be taken into consideration that this absorption does not belong to the C=N vibration, but to the whole thioguanidino group incorporated into the hetero ring. As in this case a group vibration exists, it cannot be foreseen whether conjugation will increase or decrease the frequency of this vibration. It is quite possible that conjugation will cause an increase in the frequency, as a similar influence has been described in the case of some N-acyl- and N-methyl derivatives [11]. On the other hand, the spectra of types "C" and "B" belong to thiazoline and thiazine derivatives, respectively, accordingly the shift in the frequency may be due to the hetero ring, which could affect the mesomeric system without causing a shift in the tautomeric equilibrium. Nevertheless, it is probable that the spectra of type "C" of thiazolines suggest the tautomeric structure Ia, and the "B"-type spectra of thiazines indicate structure Ib. This supposition is substantiated by the association structures, and the same conclusion could be drawn from the data obtained by other (NMR, MS) methods [17, 18].

In compounds I the NH group has acid character and should form strong hydrogen bonds. This is all the more probable as the other  $sp^2$  nitrogen atom is a proper electron donor. It may be presumed that compounds with structure I should form, at least partly, cyclic dimeric association structures (IVa and IVb) connected by strong hydrogen bonds, similarly to amidines [29] in which the same -NH-C=N- group can be found. Of such associations a broad  $\nu$ NH band is characteristic in the region between 3200 and 2700 cm<sup>-1</sup>, which is split into submaxima [28-36].

Of the tautomers, IVa should form stronger hydrogen bonds, as the aromatic substituent attached to the NH group increases the mobility of the NH protons, and the alkyl substituent affixed to the other electron-releasing nitrogen atom, increases its inclination to form a hydrogen bond. In the case of **IVb** the situation is reversed; the aryl substituent decreases the electron donor character of the exocyclic nitrogen and the alkyl group increases the basicity of the NH group, decreasing simultaneously the mobility of the protons. All this should result in weaker hydrogen bonds.



As the spectra of type "C" reveal that the cyclic dimeric associations are present to a greater extent (intense, diffuse absorption in the region  $3300 - 2600 \text{ cm}^{-1}$ ) and the "B"-type spectra indicate the predominant formation of simple intermolecular associations (weaker absorption between 3200



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and 3000 cm<sup>-1</sup>), the conclusion can be drawn that thiazines contain weaker hydrogen bonds suggesting the presence of the Ib tautomeric form, whereas in the five-membered thiazoline analogues structure Ia is probable, in accordance with the stronger hydrogen bonds.

In the spectra of 2-N-alkyl-substituted thiazolines and thiazines - similarly to the compounds of structure  $\mathbf{II}$  — there is almost no cyclic dimeric association (Figs 9 and 10) [16], as the NH group is too basic for the formation of strong hydrogen bonds.

# Experimental

The IR spectra were recorded with an UR-10 Zeiss (Jena) infrared spectrometer in KBr pellets.

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# THE STRUCTURE OF CARBETHOXY AND ACETYL DERIVATIVES OF 2-ARYLAMINO-THIAZOLINES, -THIAZINES AND 1-ARYL-2-IMINO-THIAZOLINES

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Carbethoxylation of 2-imino-3-arylthiazolidines leads to acylimino derivatives, the structures of which were proved by the low wavenumber  $(1670 \text{ cm}^{-1})$  of the carbonyl band in their IR spectra. This supports the supposed structure of the starting material, too.

Acylation of 2-arylaminothiazolines can lead theoretically to two isomers. According to the concordant IR and NMR data of the carbethoxy and acetyl derivatives, only the 2-substituted compounds are formed. In the case of the analogous thiazines the isomers can be distinguished only on account of their NMR spectra, as the carbonyl frequency being in the thiazolines always at about 1750 cm<sup>-1</sup>, varies in the spectra of the thiazines between 1745 and 1705 cm<sup>-1</sup>. The NMR data have shown that, except in one case, where a mixture of the two isomers was formed, the acyl group becomes attached always to the exocyclic nitrogen in the thiazines, too.

Our previous papers [1-4] dealt with the synthesis and structure elucidation of compounds I and II, as well as with the tautomerism of Ia  $\Rightarrow$  Ib. Compounds of structure Ia and Ib are mesomeric systems (Ia'  $\leftrightarrow$  Ia'', Ib'  $\leftrightarrow$  Ib'')



where Ia' and Ib' represent only extreme structures, but the double bond and the proton cannot be located within the thiourea group [5].



In the acylated derivatives of I no tautomerism exists, and the isomers, derived from the different tautomers, possess well defined structures (III, IV).

This paper deals with the structure elucidation of the carbethoxy and acetyl derivatives (III, IV and V, resp.) of compounds I and II based on their IR and NMR spectra. The aim of our work was to investigate whether the size of the hetero ring and the aryl substituent display any effect on the structure of the isomers formed, and whether the significant difference [5] between the spectra of thiazolines (I, n = 2) and thiazines (I, n = 3) is still existing in their acylated derivatives.

# IR investigation of the carbethoxy derivatives

In the frequencies of the C=O valence vibration ( $\nu$ C=O) of the isomers III and IV containing the same acyl group significant differences could be predicted [6]. In the case of the acyl derivative III of the tautomer Ia two further unsaturated substituents are attached to the exocyclic nitrogen atom besides the acyl group, and their additive -I effect should increase the  $\nu$ C=O frequency [6]. In the case of the simple amides – due to the delocalization of the electrons – a group frequency of mainly  $\nu$ C = O type does absorb, extending over the C-N band too [7a], consequently its frequency is smaller (amide-I band). In compounds of type III and IV mesomerism is suppressed by the electron-withdrawing substituents, consequently the  $\nu$ C=O vibration of higher frequency will absorb instead of the amide-I group frequency [6].

In the acyl derivatives IV of the tautomer Ib, a C=N double bond and an alkyl group are attached to the endocyclic nitrogen atom, in addition to the acyl carbonyl. In this case the carbonyl frequency is increased only by the electronegativity of the former substituent, consequently it should appear at lower wavenumbers compared with the isomers III. This difference in the carbonyl frequencies makes possible a decision between the isomers III and IV if the spectra of both acyl derivatives are available. In one case we succeeded in separating the two isomers and the vC=O frequency differed by 15 cm<sup>-1</sup> (see Table I). If only one of the isomers is available, structures III and IV are not distinguished by the IR spectra alone, as the vC=O frequency may be influenced to a greater extent by other differences in the structures.

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Table I

Spectroscopic data of carbethoxy derivatives III-V (Ac = -COOEt)

Struc-		n	IR [cm	<sup>-1</sup> ], (KBr)	$NMR[\delta_{TMS} = 0 \text{ ppm}], (CDCl_3)$			
ture	m		νC=0	vC=N	δArCH <sub>3</sub>	δSCH <sub>2</sub>	ðNCH <sub>2</sub>	δCCH <sub>2</sub>
ш	CH <sub>3</sub>	2	1750 vs, b	1650 s, sh	2.20	3.10	4.20	_
v		-	1670 s, sh	1555 vs, b	2.20	3.30	3.80	-
ш			1730 vs, sh	1630 s, sh	2.25	2.90	4.00	2.20
v	CII.3	3	1665 vs, sh	1525 vs, sh	2.25	3.15	3.60	2.40
ш	CI	9	1745 vs, sh	1630 s, sh	-	3.15	4.30	_
v		4	1675 vs, sh	1545 vs, b		3.35	3.90	_
ш			1745 vs, sh	1620 vs ,sh	_	2.90	3.90	2.10
IV	Cl	3	1730 vs, b	1630 s, sh		3.00	3.60	1.80
v			1675 vs, sh	1510 vs, sh	_	3.10	3.65	2.40
ш		0	1745 vs, b	1640 vs, b	2.10	3.05	4.20	
v	CH <sub>3</sub> Br-CH <sub>3</sub> CH <sub>3</sub>	2	1665 s, sh	1540 vs, b	2.10	3.30	3.75	
ш			1705 vs, sh	1615 vs, b	2.15	2.85	3.90	2,20
v		3	1645 vs, sh	1500 vs, b	2.20	3.10	3.50	2.40

vs = very strong, s = strong, sh = sharp, b = broad.

SOHÁR et al.: STRUCTURE OF CARBETHOXY AND ACETYL DERIVATIVES

In the case of II, we get acylimino derivatives V in which the delocalization of the electrons is enhanced because of the conjugation of the double bond to the carbonyl group. Consequently, an amide-I band of much lower frequency appears in the spectrum [6]. The decrease in the frequency (which can be observed in the vC=N band too, and even to a greater extent), compared with the isomers III and IV makes possible an unambiguous detection of structure V.

Three types of aryl substituents were chosen for our investigations, 2,6-dimethyl-, 2,6-dichloro- and 2,6-dimethyl-4-bromophenyl, and from the corresponding isomers I and II the carbethoxy derivatives<sup>\*</sup> were prepared in both the thiazoline and thiazine series. The IR data of these 12 compounds can be seen in Table I.

The amide I (vC=O) frequency of the carbethoxy derivatives of type V, derived from compounds II, appears at about 1670 cm<sup>-1</sup> (see, e.g., Figs 1 and 2). In the spectra of the isomers, derived from compounds of structure I, however, the vC=O band appears in the region 1750-1705 cm<sup>-1</sup>. This significant difference in the frequency is an unambiguous proof of structures I and II of the starting materials. (In the paper, dealing with the synthesis and investigation of these compounds [5] we considered the possibility of for-



\* From among the acyl derivatives the carbethoxy compounds were chosen because their vC=0 frequency is higher by 20-50 cm<sup>-1</sup> than that of the amides [7c], due to the -Ieffect of the ethereal oxygen. Consequently, this band will be properly separated from the vC=N band, which appears in the range 1650-1500 cm<sup>-1</sup>. Moreover, the carbethoxy derivatives could be easily synthesized and purified.

mation of thioamide characterized there by structure "III",\* but rejected this structure in view of the acyl derivatives whose IR data excluded this isomer. Both isomers which can be derived from the tautomers "IIIa" and "IIIb"\*\* should give a carbonyl band with a frequency higher than 1770 cm<sup>-1</sup>, as they would be cyclic monothioimide and monothiocarbonate derivatives, respectively [7b]. All of our compounds showed a much lower carbonyl frequency.)

As far as the spectra of the thiazoline and thiazine derivatives with structures III or IV are concerned, the differences observed with the basic compounds appear also here, as the carbonyl frequency of the thiazolines is somewhat higher (1750 -1745 cm<sup>-1</sup>, Fig. 3) than that of the thiazines (1745 -1705 cm<sup>-1</sup>, Figs 4 and 5; Table I). That means either that acylation of the







Fig. 5. IR spectrum of IV (Ac = carbethoxy, Ar = 2,6-dichlorophenyl, n = 3)

\* "III" refers to the numbering of the formula in Ref. [5].

\*\* "IIIa" and "IIIb" refer to the numbering of the formulas in Ref. [5].

thiazolines should give exclusively derivatives with structure III whereas acylated thiazines have structure IV, or, more probably, that the electron distribution of the thiourea group, and consequently the frequency of the attached carbonyl group, depends on the size of the ring. Of the two isomers formed simultaneously the one with the higher vC=0 frequency belongs to structure III, and the other to structure IV. In the cases where only one isomer was formed, the structure could not be proved unambiguously by this method. The  $\nu C = O$  frequencies of the thiazolines are so close to each other that all of them may be considered to have the same structure, namely III, according to the relatively high wavenumber. The thiazines, however, give very different frequencies. As the two single isomers give an equal and a lower frequency, respectively, than that of structure IV, the same formula can be taken into consideration for them too, though because of the great difference in the frequency of these two compounds  $(25 \text{ cm}^{-1})$  — which indicates the strong influence of the substituents - precaution should be taken. As a decision between structures III and IV can be made safely only in the possession of both isomers, in order to determine the structure of the single isomers further investigations (NMR spectra) were necessary.

# NMR investigation of the carbethoxy derivatives

Choice between the isomeric structures can be made by the help of any of the signals of the NMR spectra except for that of the ethyl group. This means 3-5 independent data, which may differ in the spectra of the isomers. In spite of this, great care must be exercised as the order of these differences and even their direction depend very markedly upon the molecular structure [1, 8, 9].

The use of the  $\delta NCH_2$  signal for distinguishing between tautomers Ia and Ib as well as between the isomers III and IV has been suggested earlier [10-13]. The neighbourhood of the C=N double bond will cause a paramagnetic shift of this signal in structures Ia and III. Our model experiments have shown, however, that this effect is changing, it is frequently very small, and in some pairs with proved structures even opposite shifts could be detected [8, 9, 14].

The behaviour of the  $\delta$ SCH<sub>2</sub> signal is very much similar, but the expectable difference in the shift is even smaller, often hardly significant, consequently reversed shifts do occur more often, as other effects will overcompensate the small shifts.

In our experience [14], in thiazines the signal of the central methylene group differs too, as  $\delta \text{CCH}_2(\text{III}) > \delta \text{CCH}_2(\text{IV})$ .

The  $\delta ArCH_3$  signals of the aromatic substituents carrying methyl groups in positions 2 and 6 differ similarly, as it has been found in investigations [8, 9]

carried out with some isomers III and IV with proved structures, the difference being at least 0.2 ppm ( $\delta ArCH_3$  (III)  $< \delta ArCH_3$  (IV)).

Finally, there is a difference in the structure of the  $AB_2$ -type spectrum of the ring protons, too [14, 15, 16]. In the case of the 2,6-dichloro derivatives structure III gives an  $AX_2$ -like spectrum, whereas that of structure IV is close to the type  $A_3$ . The structure of this multiplet is — unlike the other NMR and IR parameters — independent of the size of the hetero ring, as the analogous thiazoline and thiazine isomers show the same type of spectra. In the case of the 2,6-dimethyl derivatives, however, an  $A_3$ -type spectrum can be expected for isomer III. In the spectrum of the 4-bromosubstituted derivatives, the two equivalent ring protons have to give an  $A_2$ -type singlet in both isomers.

From the experimental results (see Table I), of which the spectra of the pair of isomers and that of the analogous thiazoline derivative are shown in Figs 6-8 for illustration, the following conclusions can be drawn:

1. The expected signals are present in all compounds investigated, proving the presence of the functional groups and thereby the expected structures.

2. The  $\delta NCH_2$  and  $\delta SCH_2$  signals of the thiazolines of structure V (proved by IR) are shifted paramagnetically by 0.20-0.25 ppm.

3. The  $\delta CCH_2$  signal appears in the spectra of all three models with structure V (n = 3) at 2.40 ppm; this is a difference from the spectra of the acyl derivatives derived from tautomer I, where the chemical shift of this signal is always smaller.

4. The chemical shifts of the  $\delta ArCH_3$  signals are practically identical for the carbethoxy derivatives belonging to both type I and type II in the thiazoline-thiazine pairs; the difference is smaller than 0.05 ppm.

5. The vArH multiplets in the thiazoline-thiazine pairs is practically identical, approaching an  $A_3$  type of spectra. In the case of the 2,6-dichloro derivatives it is shifted towards the type AB<sub>2</sub>.

6. In the acyl derivatives of compounds I, the  $\delta NCH_2$  signal appears for thiazolines between 4.30 and 4.20 ppm, and in thiazines between 4.00 and 3.90 ppm (except in the spectrum of the isomer whose structure was shown by IR to be IV, in which this signal appeared at 3.60 ppm). Accordingly, structure III is more probable for all compounds whose pair has not been prepared as the corresponding signal of the derivatives with structure IV is more downfield compared with the other thiazines; in the case of the thiazolines a higher value (by about 0.3 ppm, *i.e.*, 3.9 ppm) would be expected for compounds with structure IV; this is still lower than the data obtained.

7. The  $\delta$ SCH<sub>2</sub> signal appears in the thiazolines derived from structure I in the region 3.15 - 3.05 ppm, and in the spectrum of the thiazines between 2.90 and 2.85 ppm. The only compound with structure IV has a different value (3.00 ppm) which means a shift in the irregular direction.



Fig. 8. NMR spectrum of III (Ac = carbethoxy, Ar = 2,6-dichlorophenyl, n = 2)

8. The  $\delta CCH_2$  signal of the thiazines appears between 2.20 and 2.10 ppm, with the exception of the compound with structure **IV** whose corresponding signal is at 1.80 ppm.

9. The  $\delta$ ArCH<sub>3</sub> signal of each compound can be detected between 2.25 and 2.10 ppm, suggesting an analogous isomeric structure.

10. Among the 2,6-dichloro compounds the AB<sub>2</sub>-type multiplet of the ring protons is completely identical in the thiazolines and the thiazine analogue with structure III. In all the other compounds these protons give a singlet, except for the compound of structure IV, where an AB<sub>2</sub> multiplet can be observed, which is close to the A<sub>3</sub> marginal case.

All these data prove unambigously that with the exception of a single pair of isomers, only compounds of structure III are formed in the acylation of isomer I, and that carbethoxylation of II leads always to the expected acylimino derivative V.

#### IR and NMR investigation of the acetyl derivatives

As mentioned, the acetyl derivatives are less suitable models for IR investigation than the carbethoxy derivatives, as the amide-I band may sometimes overlap with the band of the  $\nu$ C=N group frequency. Nevertheless, a few such derivatives were synthesized to investigate whether or not the structures of the isomers differ from that of the carbethoxy derivatives.



Fig. 9. IR spectrum of V (Ac = acetyl, Ar = 2,6-dimethylphenyl, n = 2)

There was no need of investigating the acetyl derivatives V obtained from compounds of structure II, as no doubt arises concerning their structure. However, spectroscopically it was of some interest that the amide-I and the  $\nu C=N$  band appeared also in these compounds at low wavenumbers. For illustration, the spectrum of the 2,6-dimethyl derivative of the thiazoline of type II and that of the 2,6-dimethyl-4-bromo derivative of the thiazine of type II are shown in Figs 9 and 10, where the amide-I band appears at 1640 and 1615 cm<sup>-1</sup>, respectively, and the band of the  $\nu C=N$  group frequency at 1500 and 1400 cm<sup>-1</sup>, respectively; all the mentioned maxima are very intense.



The same models as in the carbethoxy series, derived from compounds of structure I, as well as the chloroacetyl and dichloroacetyl derivatives of the 2,6-dimethyl-4-bromo compound with thiazoline ring were investigated. The carbonyl frequencies of the thiazoline-thiazine pairs did not differ significantly and were essentially smaller than those of the carbethoxy compounds. Interestingly, neither the chloroacetyl nor the dichloroacetyl derivatives showed any increase in the frequency. For illustration the spectra of the chloroacetyl derivative of the 2,6-dimethyl-4-bromophenyl-substituted thiazoline (Fig. 11) and the acetyl derivative of the thiazine-type compound (Fig. 12) are shown.



Fig. 11. IR spectrum of III (Ac = chloroacetyl, Ar = 2,6-dimethyl-4-bromophenyl, n = 2)



Fig. 12. IR spectrum of III (Ac = acetyl, Ar = 2,6-dimethyl-4-bromophenyl, n = 3)
All these compounds were found to possess structure III according to the NMR data (see Table II\*), indicating that neither variation of the aromatic substituent, nor that of the acyl group or the size of the hetero ring leads to isomer IV. This suggests a greater stability of structure III, which may be due to electron distribution and steric factors [8, 9, 14].

## Table II

			IR [cm-	<sup>1</sup> ], (KBr)	1	NMR [	$\delta_{TMS} =$	0 ppm]	, (CDCI	3)
Ac	Ar	n	pC=0	p'C=N	ðNCH <sub>2</sub>	$\delta SCH_2$	∂CCH₂	ôArCH <sub>3</sub>	$\delta \mathrm{AcCH}_n$ n=1,2,3	ðArH
-COCH <sub>3</sub>			1690 s, sh	1650 vs, b	4.35	3.25	_	2.15	2.75	7.20
-COCH <sub>2</sub> Cl	CH <sub>3</sub>	2	1700 s, sh	1650 vs, b	4.30	3.15	_	2.10	4.90	7.10
- COCHCl <sub>2</sub>			1700 s, sh	1660 vs, b	4.35	3.20		2.10	7.95	7.15
		3	1690	1635	3.95	2.85	2.15	2.10	2.55	7.15
	CH <sub>3</sub>	2	1690 s, sh	1650 vs, b	4.21	3.05	-	2.10	2.70	7.0*
$-\operatorname{COCH}_3$	CH3	3	1690 s, sh	1635 vs, b	3.90	2.74	2.10	2.10	2.55	6.95
		3	1685 s, sh	1625 vs, b	4.05	2.95	2.15	_	2.70	AB <sub>2</sub>

Spectroscopic data of the acetyl derivatives of structure III

\* The value of the main maximum in the  ${\rm AB}_2$  multiplet well approximating the limiting case  $A_3.$ 

The results of the measurements are summarized in Table II; since the conclusions drawn from them are qualitatively identical with those mentioned in connection with the carbethoxy derivatives, no detailed explanation is

\* The 2,6-dichlorophenyl-substituted thiazoline derivative could not be purified, therefore its data are missing from the Table.

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Fig. 13. NMR spectrum of III (Ac = acetyl, 2,6-dimethylphenyl, n = 2)

given here for the suggestion of structure III. For illustration, the spectrum of the acetyl derivative of the 2,6-dimethylthiazoline is shown in Fig. 13.

## Experimental

The IR spectra were recorded on a Zeiss (Jena) doublebeam spectrometer in KBr pellets: the NMR spectra were taken at 60 MHz on a JEOL C-60 and a VARIAN A-60D spectrometer in deuterochloroform, using TMS as internal standard.

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# STUDIES ON MIXED AMINO ACID METAL CHELATES

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The Irving-Rossotti technique has been applied to study the formation constants corresponding to the reaction

$$(MA)^- + L^- \rightleftharpoons (MAL)^{2-}$$

where M=Cu, Ni;  $A = nitrilotriacetic acid; L = glycine, <math>\alpha$ - or  $\beta$ -alanine. MNTA 1: 1 complexes have been found to form at lower pH; they are stable at higher pH. The values of the formation constants obtained for the mixed ligand systems (K<sub>MAL</sub>) are by about 2.0—4.0 log units less than the first formation constant of the metal amino acid system (K<sub>ML</sub>). The relative values of the formation constants for the mixed ligand complexes of Ni(II) and Cu(II) are discussed.

Nitrilotriacetic acid is known to form complexes with a number of metal ions [1-3], which are stable at higher pH [4]. The compound behaves as a tri- [5] or quadridentate ligand [1], coordination taking place at the N and two or three  $COO^-$  groups. In the case of 1:1 NTA complexes of metal ions with high coordination number, the remaining positions may be occupied by the water molecules or hydroxide ions. If a bidentate ligand coordinating to the metal ion at higher pH is added to the 1:1-metal-NTA mixture, the vacant positions may be occupied by this ligand, resulting in the formation of mixed ligand complexes of the type M(NTA)L. The study of such systems where M = Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Pb(II); L = serine and arginine have been carried out by ISRAELI and CECCHETTI [6]. HOPGOOD and ANGELICI [4] have also studied the ternary systems with M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). A = NTA and L = amino acids and their esters, using a potentiometric titration method. In the present work the systems M(NTA)L have been investigated with M = Cu(II) or Ni(II) and L = glycine,  $\alpha$ - or  $\beta$ -alanine. The reaction can be represented by

$$\begin{array}{l} \text{MNTA} + \text{L} \rightleftharpoons \text{M}(\text{NTA})\text{L} \\ \text{K}_{\text{MAL}} = [\text{M}(\text{NTA})\text{L}]/[\text{MNTA}] [\text{L}] \end{array}$$

The formation constant  $K_{MAL}$  corresponding to the association of the amino acids with MNTA, has been determined by a modified form of the IRVING – RossorTI titration technique [7, 8].

The original method [7] is devised for studying the formation constants in systems of the type  $M + L \rightleftharpoons ML$ . If the reaction  $M + A \rightleftharpoons MA$  takes place at lower pH and MA is stable at high pH, the formation constant of the mixed ligand system  $MA + L \rightleftharpoons MAL$  can still be determined using the basic concepts of the IRVING-ROSSOTTI technique [7].

## Experimental

Glycine (Rienal, Germany),  $\alpha$ - and  $\beta$ -alanine and NTA (BDH) used were of reagent grade. Metal perchlorates were prepared in solution and their metal contents determined. Other reagents used were sodium hydroxide (Merck), sodium perchlorate (Fluka), perchloric acid (B and A). All solutions have been prepared with conductivity water.

A type E 350A Metrohm pH meter (accuracy  $\pm 0.05$ ) was employed for the pH measurements. The titrations were carried out at 25 °C, in a constant temperature bath ( $\pm 0.1$  °C).

For the mixed ligand systems the following solutions were prepared in 50 ml volume for the titrations

0.02 M HClO<sub>4</sub>, 0.002 M NTA, 0.178 M NaClO<sub>4</sub>;
 0.02 M HClO<sub>4</sub>, 0.002 M NTA, 0.002 M metal perchlorate, 0.176 M NaClO<sub>4</sub>;

(3) 0.02 M HClO<sub>4</sub>, 0.006 M HClO<sub>4</sub>, 0.002 M secondary ligand, 0.172 M NaClO<sub>4</sub>;

(4) 0.02 M HClO<sub>4</sub>, 0.002 M NTA, 0.002 M secondary ligand, 0.002 M metal perchlorate, 0.174 M NaClO4.

The ionic strength of each solution was thus initially adjusted to 0.2 M. Each of the above samples was titrated against 0.2 M NaOH. The plots of pH against the volume of alkali added are shown in Fig. 1 for the Cu/Ni(NTA) glycine system. The type of the curves is the same in the case of  $\alpha$ - and  $\beta$ -alanine, too.



Fig. 1. Potentiometric titration of nitrilotriacetic acid and glycine (ionic strength 0.2~MNaClO<sub>4</sub>, 25 °C)

## **Results and discussion**

It has been shown earlier that 1:1 CuNTA and NiNTA complexes [9] are formed at lower pH. In the present case the metal + NTA curve (2 in Fig. 1) differs from the NTA curve (1) above (2), indicating that a 1:1 MNTA complex is formed at lower pH. The horizontal distance between the two curves remains almost constant, showing that the 1:1 MNTA complex, does not dissociate at higher pH. The  $M^{2+}$  + NTA + amino acid curve(4) is not below the metal + NTA curve(2) in the lower pH range. Thus the amino acids do not combine with the metal ions in this range where  $M^{2+}$  forms a 1:1 complex with NTA. Curve(4) does not, however, exactly coincide with curve(2) but is slightly above it. This is due to the fact in the lower pH range amino acids are protonated and exist as a mixture of the species  $CH_2NH_3$ +COOH and  $CH_2NH_3$ +COO<sup>-</sup>. However, above pH ~ 6.0 curve(4) goes below curve(3). This confirms that in this range the amino acids are coordinated to MNTA, resulting in the liberation of extra hydrogen ions. The reaction can be represented as follows:

 $\begin{array}{r} \mathrm{M}^{2\,+} \,+\, \mathrm{H}_{3}\mathrm{NTA} \rightleftharpoons \mathrm{M}(\mathrm{NTA})^{-} \,+\, 3\mathrm{H}^{+} \\ \mathrm{M}(\mathrm{NTA})^{-} \,+\, \mathrm{NH}_{2}\mathrm{CH}_{2}\mathrm{COOH} \rightleftharpoons \mathrm{M}(\mathrm{NTA})(\mathrm{NH}_{2}\mathrm{CH}_{2}\mathrm{COO})^{2\,-} \,+\, \mathrm{H}^{+} \end{array}$ 

The formation of the mixed ligand complex at high pH has also been demonstrated by recording the absorption spectra of a mixture with Cu: NTA: glycine = 1:1:1 at pH ~ 9.3 and comparing it with the absorption spectra of mixtures in which Cu: gly = 1:1 and Cu: NTA = 1:1 at the same pH. There is only one maximum in the visible absorption spectrum of Cu(NTA)gly (~ 650 mµ) and it falls below those observed in the case of Cu: gly (~ 670 mµ) and Cu: NTA (~ 720 mµ) mixed in a 1:1 ratio. Similarly the absorption spectrum of the Ni(II) system reveals only one maximum at ~560 mµ for 1:1:1 mixtures of Ni, NTA and amino acids. This falls below the ones observed for Ni: glycine (~ 610 mµ) and Ni: NTA (~ 590 mµ).

The additional hydrogen ions liberated as a result of amino acid coordination can be determined from the horizontal distance between curve(4) and the amino acid curve(3), because to the amino acid samples three equivalents of extra perchloric acid have been added to compensate for the hydrogen ions liberated upon the combination of  $M^{2+}$  with NTA in the metal and NTA, and amino acid solutions. The horizontal distance between curves(4) and (3) can be used for the calculation of  $\overline{n}$ , the average number of amino acid ligands associated with one  $[M(NTA)]^-$ . The equation used for the calculation of  $\overline{n}$ is the same as in a previous paper [7].

$$ar{n} = rac{({
m V}^{\prime\prime\prime}-{
m V}^{\prime\prime})~({
m N}+{
m E}^{
m 0}+{
m T}^{
m 0}_{
m L})~({
m Y}-{
m n}_{
m H})}{({
m V}^{
m 0}+{
m V}^{\prime\prime})~{ar{
m n}}_{
m H}\cdot{
m T}^{
m 0}_{
m m}}$$

In the above equation V" and V''' are the volumes of alkali added to reach the same pH in the secondary ligand curve and in the MNTA + secondary ligand curve, respectively. V<sup>0</sup> is the initial volume of the solution, N — the concentration of alkali, E<sup>0</sup> — the concentration of mineral acid and T<sup>0</sup><sub>L</sub> is the initial ligand concentration. T<sup>0</sup><sub>m</sub> is the concentration of  $[M(NTA)]^-$  which is equal to the concentration of metal salt used. pL values were also calculated using the equation given in a previous paper [7]. Values of  $\bar{n}_{\rm H}$  and proton ligand stability constants were taken from our earlier investigation under similar conditions [10]. Formation curves were drawn by plotting  $\bar{n}$  against pL in the range pH  $\sim 6-7.5$ . At  $\bar{n} = 0.5$  of the formation curve, pL =  $= \log K_{MAL}$ . More precise values were obtained by plotting pL at each point against  $\log (1 - \bar{n})/\bar{n}$ , which gave a straight line. The average values thus obtained are listed in Table I. The values for the Cu(NTA)gly and Ni(NTA)gly

## Table I

Logarithms of the stability constants of ternary  $M^{2+}-NTA$ -ligand complexes ( $\mu = 0.2 \ M; \ 25 \,^{\circ}C$ )

$\log {\rm K}_{\rm Cu(NTA)}^{\rm Cu(NTA)}$	log K <sub>Ni(NTA)</sub> L
$5.61 \pm 0.04$	$4.88\pm0.04$
$5.76\pm0.05$	$4.72\pm0.04$
$5.03\pm0.04$	$3.76 \pm 0.08$
	$\frac{\log \kappa_{Cu(NTA)}^{Cu(NTA)}}{5.61 \pm 0.04}$ 5.76 \pm 0.05 5.03 \pm 0.04

systems, though not in exact agreement with the results of ISRAELI and CECCHETTI [6], are very close to the values reported by HOPGOOD and ANGELICI [4].

The K<sub>MAL</sub> values for the association of the amino acids with CuNTA and NiNTA are much lower (by about 4.0-2.0 log units) than the first formation constants, K<sub>ML</sub>, corresponding to the association of the amino acids with the metal ions [8, 11]. K<sub>MAL</sub> is even lower than the second formation constant K<sub>ML<sub>2</sub></sub> [4, 11]. Thus K<sub>MAL</sub>, where A is a charged ligand (nitrilotriacetate), is much less than K<sub>ML</sub>, where A is a neutral ligand (dipyridine). The values of  $K_{MAL}$  in the latter case are [8] almost equal to  $K_{ML}$ , and the reason has been explained. Lower values of K<sub>MAL</sub>, with ionic A have been observed by earlier workers too [11]. The reason is the greater tendency of L<sup>-</sup> to bind with [M(aq)]<sup>2+</sup> than with [(MA)]<sup>-</sup>, owing to electrostatic repulsion with the latter. This results in K<sub>MAL</sub> < K<sub>ML1</sub>. The fact that K<sub>MAL</sub> < K<sub>ML2</sub> also needs explanation.  $L^-$  should have a lesser tendency to combine with  $[M(L)]^+$ because of the electrostatic repulsion due to the L<sup>-</sup> already bonded. This repulsion can, however, be expected to be less than the repulsion between A<sup>3-</sup> and L<sup>-</sup>. Further A<sup>3-</sup> will occupy more space around the metal ions. As a result of this  $K_{MAL}$  is lower than even  $K_{ML_{*}}$ .

The order of the formation constants corresponding to the association of amino acids with MNTA is the same as in simple Cu amino acid or Ni amino acid systems [9].  $K_{MAgly} \approx K_{MA\alpha \cdot ala} > K_{MA\beta \cdot ala}$ . The order cannot be explained in terms of the basicities of the ligands alone. Although more basic  $\beta$ -alanine forms a less stable complex. This is because it forms a less stable six-membered ring [12].  $\alpha$ -alanine, though slightly more basic than glycine, forms a less stable complex. Both amino acids are similar in structure and form fivemembered rings. IRVING and PETTIT [13] have explained the difference in terms of the fact that in  $\alpha$ -alanine methyl substitution on the carbon atom distorts the bond angle and forces the chelate ring into a less favourable conformation. As a result of steric factor,  $\alpha$ -alanine forms less stable complexes than glycine.

It is, however, observed that though the formation constants of the copper complexes differ from those of the nickel chelates by 2.0 log units in binary systems, the differences in the respective ternary systems are very small. The above observation can be explained in terms of JAHN-TELLER distortion [14]. The Cu(II) complexes  $(\alpha^3)$  are more stable than the Ni(II) chelates (d<sup>8</sup>) because the JAHN-TELLER distortion brings in additional stability in the copper complexes. This indicates that ligands along the z axis are at a greater distance than those in the equatorial plane. It can naturally be expected that if the incoming ligand has to occupy a position along the z axis, it will be held more loosely by the metal ion owing to the distorted structure. The formation constants corresponding to the coordination of that ligand will have a lower value. Nitrilotriacetic acid is regarded as tridentate [5] or quadridentate [1] and hence must occupy three positions around the Cu(II) ion in the xy plane. In the absence of the JAHN-TELLER effect, as in the case of Ni(II) complexes, the ligands along the z axis are held at the same distance as those in the xy plane, whereas in distorted Cu(II) complexes, the secondary ligand is at a larger distance. This is the reason why  ${
m K}_{{
m Cu(NTA)L}} pprox$  $\approx \mathrm{K}_{\mathrm{Ni(NTA)L}}$ . The overall value of the formation constant,  $\log \mathrm{K}_{\mathrm{MA}} + \log \mathrm{K}_{\mathrm{MAL}}$ , is much higher for Cu(II) than for Ni(II) complexes, showing that the JAHN-TELLER distortion results in an overall stabilization of Cu(II) complexes. The values of the formation constants corresponding to the association of nitrilotriacetic acid in the case of Cu(II) and Ni(II) were taken from the literature [9, 15], the sums  $\log K_{MA} + \log K_{MAL}$  being shown in Table II.

Ligand (L)	$\frac{\log K_{Cu\cdot NTA} +}{+\log K_{Cu\cdot NTA\cdot L}}$	$\frac{\log K_{Ni\cdot NTA} +}{+\log K_{Ni\cdot NTA\cdot L}}$
Glycine	18.57	16.42
α-alanine	18.72	16.26
$\beta$ -alanine	17.96	15.30

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	51	n		64	 ε.	а.
	~	**	ж	~	 а,	м.

It is also observed that there is a smaller difference between the stabilities of  $Cu(NTA)\alpha$ -alanine and  $Cu(NTA)\beta$ -alanine, than between those of the corresponding ternary Ni(II) complexes. The difference in the values of formation constants of  $\alpha$ -alanine and  $\beta$ -alanine complexes with Cu(II) and Ni(II) in binary systems are, however, almost equal. As discussed earlier,  $\beta$ -alanine forms a less stable complex than  $\alpha$ -alanine because of the formation of a sixmembered ring with greater strain. However, in the  $[Cu(NTA)(L)]^{-}$  complex, distortion causes the ligand to span more. A ligand molecule with a longer chain will be subject to lesser strain. As such,  $\beta$ -alanine will be favourably placed and the difference between the values of the formation constants of  $Cu(NTA)\alpha$ -alanine and  $Cu(NTA)\beta$ -alanine will be narrowed down. In the absence of distortion in nickel complexes, no such effect is observed in the ternary systems.

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# ON THE MOLECULAR STRUCTURE OF N,N'-THIO-BIS(DIMETHYLAMINE) AS STUDIED BY ELECTRON DIFFRACTION

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The gas phase molecular structure of N,N'-thio-bis(dimethylamine),  $(CH_3)_2NSN$   $(CH_3)_2$ , was studied by electron diffraction. A least squares refinement yielded the following bond lengths and angles: C—N 1.473  $\pm$  0.006 Å, S—N 1.688  $\pm$  0.006 Å, S—N—C 117.9  $\pm$  0.6°, C—N—C 116.5  $\pm$  1.6°, N—S—N 114.5  $\pm$  1.6°. The prevailing internal rotational form found is analogous to those of gaseous  $(CH_3)_2NSON(CH_3)_2$  and  $(CH_3)_2NSO_2Cl$ , and crystalline  $(CH_3)_2NSO_2N(CH_3)_2$ . Some tendencies of changes in the sulfur and nitrogen bond configurations are discussed.

## Introduction

The molecular structures of a series of sulfur-nitrogen compounds in the vapor phase are studied in this laboratory using the electron diffraction sectormicrophotometer method. The main purpose of these studies is to investigate how the sulfur atom in different valence states affects the trivalent nitrogen bond configuration.

As was shown in Ref. [1], the trivalent nitrogen atom bond configuration changes from peaked pyramidal to planar, depending on the nature of atoms bound to the nitrogen atom. In particular, the comparison of the nitrogen bond configurations in some siliccn, phosphorus, sulfur and chlorine derivatives shows that the nitrogen configuration changes from planar to peaked pyramidal upon going from silicon to chlorine [2]. The nitrogen bond angles were found to increase upon going from  $(CH_3)_2NPOCl_2$  to  $(CH_3)_2NPCl_2$  or from  $(CH_3)_2NSO_2Cl$ to  $(CH_3)_2NSON(CH_3)_2$ . On the basis of this trend, a close to planar nitrogen configuration was predicted in Ref. [2] for N,N'-thio-bis(dimethylamine),  $(CH_3)_2NSN(CH_3)_2$ . A first account of the electron diffraction study of  $(CH_3)_2NSN(CH_3)_2$  has already been published [3] with results obtained using constant scattering factors and mainly a trial and error structure analysis. The present paper outlines only briefly the procedure described in detail in Ref. [3] and gives a more complete determination of the nitrogen and sulfur bond configuration.

## Experimental

The sample of  $(CH_3)_2NSN(CH_3)_2$  was prepared by PÁLDI (Research Group for Inorganic Chemistry of the Hungarian Academy of Sciences). The purity of the sample was checked by gas-chromatography and elemental analysis [4].

The electron diffraction patterns were taken with an EG-100A unit of this laboratory. Some parts of the unit were modified and a new nozzle system was constructed as described in Ref. [3]. Data were obtained from 19, 42 and 76 cm camera distances using 60 kV electrons and  $r^3$  sector. The experimental molecular intensities are shown in Fig. 1. Curves E of Fig. 2 and 3 are experimental radial distributions.



Fig. 1. Molecular intensities. E – experimental, T – theoretical computed from the parameters shown in Table I for a 7:3 mixture of forms I and II (see Fig. 5)



Fig. 2. Radial distributions. E – experimental, T – theoretical computed from the parameters shown in Table I for a 7:3 mixture of forms I and II (see Fig. 5). In computing the experimental curve, theoretical sM(s) values were used for the unobserved range  $0.25 \le s \le 4.50$ 



Fig. 3. Radial distributions. E – experimental, 1 through 5– theoretical for the ratios 10:0, 8:2, 7:3, 6:4 and 5:5 of forms I and II, respectively. In all computations sM(s) values of the range  $4.75 \le s \le 32.75$  were used only

## Structure analysis

Compilation of the starting structure (Table I). The values for the C-N and S-N bond lengths were obtained by a least squares refinement based on the experimental radial distribution. A preliminary value of 118.4° was estimated for the S-N-C angle considering the maximum at about 2.7 Å because of the largest weight of the S...C nonbonded distances in this region. In addition to the S...C distances, also the  $C_{11} \ldots C_{12}, C_{21} \ldots C_{22}$ and  $N_1 \ldots N_2$  distances (Fig. 4) contribute to this maximum. The N...C



Fig. 4. Labelling of the C<sub>2</sub>NSNC<sub>2</sub> skeleton

non-bonded distances contribute to the maximum at about 3.5 Å on the radial distribution curve. The  $C_{11} \ldots C_{21}$  and  $C_{12} \ldots C_{22}$  distances appear either in the same maximum or above 4 Å together with the distances  $C_{11} \ldots C_{22}$  and  $C_{12} \ldots C_{21}$ , depending on the bond angles and the internal rotational forms.

For most of the models  $C_{2v}$  symmetry was assumed. Fig. 5 shows two molecular models with  $C_{2v}$  and one with  $C_s$  symmetry. The corresponding



Fig. 5. Models and Newman projections for the internal rotational forms I, II and I/II

Newman projections are also shown. By varying the C-N-C and N-S-N angles and the internal rotational forms around the S-N bond and later also the S-N-C angle, we arrived at the values shown in the starting structure. Form I of Fig. 5 was found to be the prevailing internal rotational form while the presence of forms II and I/II could not be excluded.

Refinement. The further refinement was carried out during our visit to the Center for Structural Studies of the University of Texas (Austin, Texas, USA). In these calculations the

$$g_{ij/BT}(s) = (|f_i(s)| |f_j(s)| \cos [\eta_i(s) - \eta_j(s)])/I_b^T(s)$$

scattering functions were used. Here |f(s)| and  $\eta(s)$  are the absolute values and phases of the complex electron scattering amplitudes and  $I_b^T(s)$  is the theoretical background.

At first, theoretical radial distributions were computed for different ratios of forms I and II (Fig. 5) and compared with the experimental radial distribution. Fig. 3 shows some of the curves. Both the experimental and theoretical radial distributions were obtained by Fourier transformation of the corresponding sM(s) molecular intensity data in the interval of s = 4.75to 32.75 Å<sup>-1</sup>. The lack of small angle experimental data does not permit a detailed study of the internal rotational forms. However, it seems safe to conclude that the external part of the theoretical curve computed for the 70% + 30% ratio of forms I and II approximates the experimental radial distribution somewhat better than those where the corresponding ratio was 80% + 20% or 60% + 40%. It is noteworthy, however, that in calculating the radial distributions, the same amplitudes of vibration were used for both forms, whereas the N...C non-bonded distances decisive in studying the rotational forms, are expected to have larger amplitudes for form I than for form II.\* Thus the N . . . C distances in form II would have had a lesser effect on our theoretical radial distributions than if the appropriate amplitudes had been used. This, in turn, suggests that if we find 30% of form II, using the procedure described, a value below 30% is more probable than one above it.

The final refinement of the bond lengths and bond angles based on the experimental molecular intensities was performed using SEIP's least squares refinement program [6]. A model consisting of the two forms, I and II, was used with the weights 0.7 and 0.3, respectively. The results of this refinement are shown in Table I. The uncertainties indicated contain both the standard deviation from the least squares refinement and the experimental error. The correlation coefficients for some important parameters and the scale factor (q) are shown in Table II. Concerning the amplitudes of vibration, l(C-H) was

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<sup>\*</sup> The amplitude of vibration of the non-bonded distance characteristic for the internal rotation will be much larger in the syn than in the anti conformation (see e.g.  $S_2Cl_4$  [5]).

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### HARGITTAI HARGITTAI: STRUCTURE OF N,N'-THIO-BIS-(DIMETHYLAMINE)

Refinement of th	Refinement of the bond lengths and bond angles							
	Starting structure	Results						
r(C-H), Å	1.10 (assumed)	1.10 (assumed)						
r(C-N), Å	1.474	$1.473 \pm 0.006$						
r(S-N), Å	1.686	$1.688 \pm 0.006$						
H-C-H and H-C-N	109.5° (assumed)	109.5° (assumed)						
C-N-C	116°	$116.5\pm1.6^{\circ}$						
S-N-C	118.0°	$117.9\pm0.6^\circ$						
N-S-N	116°	$114.5\pm1.6^{\circ}$						

Table I

assumed to be 0.08 Å. The values of  $0.06 \pm 0.01$  Å,  $0.06 \pm 0.01$  Å and  $0.08 \pm 0.01$  Å were obtained for l(C-N), l(S-N) and l(S...C), respectively.

	Correlation coefficients for some parameters ( $ imes 1000$ )									
	r(S—N)	SNC	r(CN)	C—N—C	N-S-N	l(S—N)	l(CN)	l(SC)	ą	
r(S-N)	1000									
s-n-c	-529	1000				21				
r(C-N)	184	- 398	1000							
C-N-C	126	36	187	1000						
N-S-N	- 2	-462	- 6	-526	1000					
l(S-N)	17	27	-362	-258	136	1000				
l(C-N)	329	-209	- 53	-158	122	168	1000			
l(SC)	- 3	104	-182	-102	-110	222	161	1000		
q	158	-153	-291	-481	294	503	432	430	1000	

### Table II

Discussion

Bond distances. The value obtained for the S-N bond is somewhat less than that calculated for the single bond (1.74 Å) using the SCHOMAKER-STEVENSON equation [7]. The S-N bond distance in  $(CH_3)_2NSN(CH_3)_2$  is the same within the uncertainties as that in  $(CH_3)_2NSON(CH_3)_2$ . However, this may well not be an indication of equal bond strengths in these two molecules. On the basis of numerous experimental data TRUTER [30] has postulated different covalent radii and electronegativities for sulfur atoms in different valence states, *i.e.*, S(II), S(IV) and S(VI). The tetravalent sulfur bonds are usually longer than those of S(II) and S(VI). The C-N bond distances in  $(CH_3)_2NSN(CH_3)_2$  and  $(CH_3)_2NSON(CH_3)_2$ are close to that in  $(CH_3)_3N$  [8]. As has been noted [9], the  $H_3C-N <$  bond length varies very little when the nitrogen bond configuration changes from planar to pyramidal.

The sulfur bond angle. The N-S-N bond angle determined in  $(CH_3)_2$ NSN $(CH_3)_2$  is larger than those in most other molecules of two-coordinated sulfur. There are some cases with double bonds where this angle is even larger, e.g., in SO<sub>2</sub> (118°59') [10],  $CH_3-N=S=O$  (121°) [11] and O=S=N in S<sub>2</sub>N<sub>2</sub>O<sub>3</sub> (115.3°) [12]. The sulfur bond angles were summarized e.g., in a review by ABRAHAMS [13] and more recently in a book edited by NICKLESS [14].

The comparison of X-S-X bond angles  $(X=CH_3, Cl, N(CH_3)_2)$  in analogous  $SX_2$ ,  $SOX_2$  and  $SO_2X_2$  molecules (see Table III) shows the following.

**Table III** 

X-S-X bond angles in the  $SX_2$ ,  $SOX_2$  and  $SO_2X_2$  molecules

x	SX <sub>2</sub>	$SOX_2$	$\mathrm{SO}_2\mathrm{X}_2$
CH <sub>3</sub> Cl N(CH <sub>3</sub> ) <sub>2</sub>	$egin{array}{rll} 98^{\circ}52'\pm10'{ m MW}[16]\ 103.0\pm0.4^{ m o}{ m ED}[17]\ 114.5\pm1.6^{ m o}{ m ED}{ m this}{ m work} \end{array}$	96°23' MW [18] 96.1 ± 0.7° ED [19] 96.9 ± 1.7° ED [2]	$egin{array}{llllllllllllllllllllllllllllllllllll$

MW - microwave spectroscopy, gas phase,

ED - sector-microphotometer electron diffraction, gas phase,

XD - X-ray diffraction, crystal phase.

While the sulfur bond angles in sulfides and sulfones show a great variation depending on the different substituents, very little variation is observed with the analogous sulfoxides. The bond angles in sulfoxides are always smaller than the analogous ones in sulfides and sulfones.

Nitrogen bond configuration. Data for the nitrogen bond angles in some silicon, phosphorus, sulfur and chlorine derivatives are collected in Table IV.

Table IV

Nitrogen bond angles in some silicon, phosphorus, sulfur and chlorine derivatives

N(SiH <sub>2</sub> ) <sub>2</sub> [2]	21	(CH <sub>2</sub> ),NPCl <sub>2</sub>	[25]	[(CH <sub>2</sub> ) <sub>2</sub> N]S this work	NCl.	[27]
120°		120°		S-N-C 117.9°	107	.1°
CH <sub>3</sub> N(SiH <sub>3</sub> ) <sub>2</sub> [2	3]	$[(\mathrm{CH}_3)_2\mathrm{N}]_3\mathrm{P}$	[26]	C-N-C 116.5°	$CH_3NCl_2$	[28]
120°		P-N-C 119.	5°	$[(CH_3)_2N]_2SO$ [2]	108	0
CH <sub>3</sub> ) <sub>2</sub> NSiH <sub>3</sub> [24	4]	C-N-C 113.	5°	S-N-C 116.1°	$(CH_3)_2NCl$	[28]
Si-N-C 120.4°		$(CH_3)_2NPOCl_2$	[25]	C-N-C 113.9°	107	0
C-N-C 111.1°		116°		$(CH_3)_2 NSO_2 Cl$ [1]	F <sub>2</sub> NCl	[29]
				112°	Cl-N-F	105°
	1				F-N-F	103°

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All these data refer to gas phase studies by electron diffraction. It is particularly important to emphasize the phase when discussing the nitrogen bond configuration. (The inversion energies of ammonia and its simple derivatives are known to be small and can be commensurable with, or exceeded by, the lattice energy or the energy of the hydrogen bond.) The trends of the changes in nitrogen bond configuration are in agreement with the GILLESPIE theory [15], according to which, the nitrogen bond angles decrease with increasing electronegativity of the group linked to the nitrogen.



Fig. 6. Newman projections of the rotational forms in (CH<sub>2</sub>)<sub>2</sub>NSN(CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NSON(CH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>Cl

The prevailing form of internal rotation. The prevailing internal rotational form found for (CH<sub>3</sub>)<sub>2</sub>NSN(CH<sub>3</sub>)<sub>2</sub> (form I) is analogous to those of gaseous (CH<sub>3</sub>)<sub>2</sub>NSON(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>Cl, and crystalline (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>, shown in Fig. 6. There is also strong indication for other rotational forms present in the vapors of  $(CH_3)_2NSN(CH_3)_2$ .

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# BENZAZEPINES, V\*

## FURTHER STUDIES ON 2,3-DIHYDRO-1*H*[1,5] BENZODIAZEPINES AND 2,3-DIHYDRO-[1,5]BENZOTHIAZEPINES

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2,3-Dihydro-[1,5]benzodiazepines and -thiazepines can be prepared by condensation of o-phenylenediamines or o-aminothiophenols with a variety of  $\beta$ -substituted ketones. The dihydro derivatives can be reduced to tetrahydro compounds; both are readily acylated. Dihydropyrimidino- and dihydropyridinodiazepines have also been prepared.

A variety of  $\beta$ -substituted ketones react with o-phenylenediamines or o-aminothiophenols to give heterocyclic seven-membered ring compounds.

We have reported previously [1, 2, 3] that 2,3-dihydro-1*H*-[1,5]benzodiazepines (I) and 2,3-dihydro-[1,5]benzothiazepines (II) can be prepared by the reactions of  $\beta$ -tert.-aminoketones with o-phenylenediamines and o-aminothiophenols, respectively.



Further examples of such heterocycles and also dihydropyridinodiazepines have now been prepared to demonstrate the generality of the method, which has wide scope because of the ready availability of the aminoketones by the Mannich reaction.

Quinoxalines have been synthesized by the reaction of o-phenylenediamines with  $\alpha$ -bromoacetophenone [4].  $\beta$ -chloropropiophenone reacts similarly with an o-phenylenediamine, to give a dihydrodiazepine (I; R<sub>1</sub> = Ph, R<sub>2</sub> = H, R<sub>3</sub> = 4,5-diMe). Since  $\beta$ -haloketones are less readily available than  $\beta$ -tert.aminoketones, this method has less general application.

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Some dihydrobenzodiazepines and a dihydrobenzothiazepine have also been prepared by reactions between  $\beta$ -hydroxyketones and o-phenylenediamines or o-aminothiophenols. When  $\beta$ -hydroxyvinylketones were used, cyclization to a diazepine did not take place, confirming earlier work by RIED et al. [5]. Instead a  $\beta$ -ketoimine was formed, which, when heated under reflux in xylene for prolonged time, was converted into a benzimidazole:



A number of dihydrobenzodiazepinones [5-13] and dihydropyridinodiazepinones [14-15] have been synthesized by condensation of 1,2-diamino compounds with  $\beta$ -ketoesters. Dihydropyrimidinodiazepinones as well as further examples of dihydrobenzodiazepinones and dihydropyridinodiazepinones have now been prepared in this way. In the case of dihydropyridinodiazepines it has been suggested [14-15] that they have structures corresponding to III (Z=N) rather than to IV (Z=N).



The product from 2-amino-4-nitro-N-( $\beta$ -diethylaminoethyl) aniline and ethyl 3,4,5-trimethoxybenzoylacetate has the unconjugated structure V rather than VI, since the IR spectrum shows the absence of N-H bonds.



When, however, the  $\beta$ -diethylaminoethyl group is replaced by a 3-picolyl or a  $\beta$ -(2-pyridyl)ethyl group, a characteristic N—H absorption is present at 3350 cm<sup>-1</sup>; replacement of the nitro group by a hydrogen atom in the latter compounds produces no change.

The dihydrobenzodiazepines (I) and dihydrobenzothiazepines (II) can be reduced to tetrahydro derivatives catalytically (Pd/C), or by sodium borohydride, or lithium aluminium hydride. The diazepinone derivatives (III; Z=CH) are, as would be expected, unaffected by sodium borohydride, but are reduced by lithium aluminium hydride to give products identical with those obtained by reduction of the appropriate dihydrobenzodiazepines.

Both dihydro- and tetrahydrobenzodiazepines can be acylated with acetyl chloride, acetic anhydride or chloroacetyl chloride to give N-acyl derivatives. The tetrahydrobenzodiazepines can also be converted into N,N<sup>2</sup>diacyl derivatives.

## Experimental

Melting points were taken on a Boetius apparatus and are uncorrected.

Infrared spectra were taken on a Beckman IR-4 spectrometer and the ultraviolet spectra on a Beckman D 2400 Model.

NMR spectra were determined with a Varian A-60 spectrometer, using TMS as internal standard.

General methods for the preparation of di- and tetrahydrobenzazepines (thiazepines, diazepines) are described below.

## **Dihydro derivatives**

(Tables I-III)

## Method A (from $\beta$ -aminoketones)

Various 2,3-dihydro-[1,5]benzothiazepines and 2,3-dihydro-1H-[1,5]benzodiazepines were prepared according to literature methods [1-3], by heating equimolar proportions of *o*-substituted (SH or NH<sub>2</sub>) anilines and  $\beta$ -aminoketones in an apolar solvent (e.g., benzene, toluene, or xylene).

### Method B (from $\beta$ -chloropropiophenone)

### 2,3-Dihydro-7,8-dimethyl-4-phenyl-1H-[1,5]benzodiazepine (1)

A solution of 13.8 g (0.1 mole) 4,5-dimethyl-o-phenylenediamine and 16.8 g (0.1 mole)  $\beta$ -chloropropiophenone in 100 ml abs. EtOH was refluxed in the presence of 10 g anhydrous sodium acetate under nitrogen for 2 hrs. The yellow product was filtered off after cooling, and washed to remove NaCl, to yield 21.2 g (85%) of 1. The crude product was recrystallized from aqueous [ethanol to give pure 2,3-dihydro-7,8-dimethyl-4-phenyl-1H-[1,5]benzodiazepine m.p. 137—138 °C; IR cm<sup>-1</sup> (KBr): 3300 (s) (NH), 1625 (s) (C=N); NMR spectrum  $\delta$ (CDCl<sub>3</sub>) 2.2 (singlet) (6H), 2.98 (multiplet) (2H), 3.72 (multiplet) (2H) and 3.39 (singlet) (1H) ppm.

### Method C (from $\beta$ -hydroxyketone)

# N-[2,3-Dihydro-7,8-dimethyl-4-(4-nitrophenyl)-1*H*-[1,5]henzodiazepine-3-yl] acetamide (12)

A solution of 13.6 g (0.1 mole) 4,5-dimethyl-o-phenylenediamine and 25.2 g (0.1 mole)  $\beta$ -hydroxy- $\alpha$ -acetamido-*p*-nitropropiophenone in 300 ml xylene was refluxed, as described in Method A, for 6 hrs.; 3.6 g (0.2 mole) of water was collected.

The resulting orange solid was filtered off and dried to give 27.4 g (78%) of **12.** A small sample was crystallized from EtOH for analysis, m.p. 205-207 °C; IR cm<sup>-1</sup> (KBr): 3400, 3380 (m) (NH), 1650-1640 (s) (CO).



No.	R	$\mathbf{R}_2$	Rg	Z	Method
1		н	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	A B
2		н	7-СООН	СН	A
3	F	Н	$7,8(CH_3)_2$	СН	A
4		Н	Н	N	A
5		Н	$7 \mathrm{CH}_3$	СН	A
6		${ m CH}_3$	$7,8(CH_3)_2$	СН	A
7		н	$7,8(CH_3)_2$	СН	A
8	OH <sub>3</sub> C	Н	$7 \ \mathrm{CH_3}$	СН	A

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				Analysis, %					
M.p., °C	Formula	С	н	N	Cl	CH <sub>3</sub> O			
	(Molecular weight)	Caled Found							
	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub>	81.56	7.25	11.19					
137-138	(250.35)	81.76	7.11	11.11	_	-			
260	$\mathrm{C_{16}H_{14}N_{2}O_{2}}$	72.16	5.30	10.52					
300	(266.30)	72.28	5.40	10.75	-	_			
154 154	$C_{17}H_{17}FN_2$	76.10	6.38	10.44					
154-156	(268.33)	76.34	6.49	10.60	_				
105 100	$C_{15}H_{15}N_{3}O$	71.13	5.96	16.59	_	12.25			
125 - 126	(253.31)	71.09	6.03	16.77		12.37			
907 900	$\mathrm{C_{15}H_{15}N_{3}O.2HCl}$	55.23	5.25	12.88	21.74	9.51			
207-208	(326.23)	55.25	5.38	12.94	21.32	9.83			
104 105	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O	76.67	6.81	10.52	_	11.66			
194 - 195	(266.34)	76.15	6.80	10.65		11.80			
100 100	$C_{19}H_{22}N_2O$	77.52	7.53	9.52	_	10.54			
118-120	(294.40)	77.57	7.56	9.26		10.27			
						C <sub>2</sub> H <sub>5</sub> C			
102-103	$C_{10}H_{22}N_2O$	77.52	7.53	9.52		15.30			
174-175	(294.40)	77.55	7.40	9.61		15.26			
	C.H. N.O.	72.95	6.80	9.45	_	20.94			
125 - 126	(296.37)	72.70	7.02	9.38		21.12			
	the stand of the state of the s	A				1 1 1			



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Mar Section				Analysis, %					
М.р., °С	Formula (Molecular weight)	С	н	N	Cl	CH <sub>3</sub> O			
mp., c	(Molecular weight)	Calcd Found							
300	C <sub>17</sub> H <sub>1s</sub> N <sub>2</sub> O (266.34)	76.67 76.72	6.81 6.98	10.52 10.47	-	-			
350	C <sub>23</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> (358.44)	77.07 77.03	6.19 6.21	7.81 7.82	-				
241-242	$\frac{C_{17}H_{15}CIN_4O_3}{(358.76)}$	56.91 56.85	4.21 4.34	15.62 $15.54$	9.88 9.84	_			
205-207	$C_{19}H_{20}N_4O_3$ (352.39)	64.76 64.60	5.72 5.82	15.90 15.97	-	_			
115-117	C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> (300.41)	83.97 83.82	6.71 6.47	9.32 9.44		-			
176-179	C <sub>21</sub> H <sub>20</sub> N <sub>2</sub> (300.41)	83.97 83.81	6.71 6.67	9.32 9.25	_	-			
43-44	$\begin{array}{c} {\rm C_{14}H_{14}N_{2}S}\\ (242.34)\end{array}$	69.39 69.17	5.82 5.62	11.56 $11.36$	-	S% 13.23 13.38			
139–141	C <sub>19</sub> H <sub>20</sub> N <sub>2</sub> (276.38)	82.57 82.37	7.29 7.05	10.24 10.26		-			
130-131	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O (306.41)	78.40 78.50	7.24 7.21	9.14 9.24		10.13 10.17			



No.	R <sub>1</sub>	R <sub>2</sub>	Method	М.р., °С	Formula (Molecular weight)
18		Н	A	115-117	$C_{15}H_{12}FNS$ (257.33)
19		Н	A	128 - 129 105 - 107	$\begin{array}{c} {\rm C_{16}H_{15}NOS} \\ (269.37) \\ {\rm C_{16}H_{15}NOS.HCl} \\ (305.83) \end{array}$
20		${ m CH}_3$	A	$105\!-\!107$	C <sub>17</sub> H <sub>17</sub> NOS.HCl (319.85)
21	OCH3	Н	A	97— 98	$C_{16}H_{15}NOS$ (269.37)
22	но	Н	A	151 - 152	$C_{15}H_{13}NOS$ (255.34)
23	ОН		A	205 - 207	$C_{21}H_{17}NO_2S$ (347.44)
24	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	Н	A	135 - 136	$C_{18}H_{19}NO_3S$ (329.42)

		Anal	ysis, %		
C	н	N	Cl	S	CH <sub>3</sub> O
		– C F	alcd		
70.01	4.70	5 44		12.46	-
70.11	4.87	5.60	-	12.59	
71.34	5.62	5.20	_	11.90	11.52
71.36	5.50	5.18		11.92	11.42
62.84	5.27	4.58	11.60	10.48	10.15
62.94	5.20	4.66	11.45	10.35	10.05
63.84	5.67	1 39	11.00	10.02	0.64
63 70	5.67	4.30	10.09	0.82	9.04
05.10	5.07	4.29	10.90	9.02	9.40
71.34	5.62	5.20		11.90	11.52
71.30	5.70	5.40		11.64	11.38
70.56	5.13	5.49		12.56	
70.53	5.15	5.29		12.45	-
				*	
72.60	4.93	4.03		9.23	_
72.62	4.74	3.98		9.42	
65.64	5.81	4.25	and the second	9.73	28.26
65.83	5.79	4.05	-	9.89	. 28.12
					14

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## HIDEG, HANKOVSZKY: BENZAZEPINES, V

No.	R <sub>1</sub>	$\mathbf{R}_2$	Method	М.р., °С	Formula (Molecular weight)
25		-NH-CO-CH <sub>3</sub>	C	167-168	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S (341.39)
26		Н	A	38— 39	C <sub>19</sub> H <sub>15</sub> NS (289.40)
27	N=		A	105-108	C <sub>17</sub> H <sub>15</sub> NS (265.38)



28	 н	F	78-81 102-104	$C_{15}H_{14}FNS$ (259.35) $C_{15}H_{14}FNS.HCl$ (295.81)
29	Н	F	77-78 141-143	$C_{16}H_{17}NOS$ (271.38) $C_{16}H_{17}NOS.HCl$ (307.84)

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		Analy	ysis, %	Analysis, %					
С	н	N	Cl	S	CH <sub>3</sub> O				
		Ca Fe	led. ound						
59.81	4.43	12.31		9.39					
60.02	4.12	12.39		9.26					
78.86	5.22	4.84		11.08					
79.06	5.32	4.79	-	11.12	-				
76.94	5.70	5.28		12.08					
77.01	5.83	5.29	T	12.01					

69.47	5.44	5.40		12.37	
69.44	5.64	5.15		12.38	
60.91	5.11	4 71	11.98	10.84	
60.87	5.15	5.02	11.92	10.92	-
70.81	6.31	5.16		11.82	11.44
70.74	6.55	5.20		11.75	11.22
62.43	5.89	4.55	11.52	10.41	10.80
62.57	5.64	4.84	11.34	10.62	10.54

## HIDEG, HANKOVSZKY: BENZAZEPINES, V



No.	R,	R <sub>3</sub>	R <sub>4</sub>	Q	Z	Method
30		7 CI	Н	СН	СН	E
31		7 CH <sub>3</sub>	Н	СН	СН	E
32		7,8(CH <sub>3</sub> ) <sub>2</sub>	Н	СН	СН	E
33		$7 \ \mathrm{NO}_2$	Η	СН	СН	E
34		Н	Н	СН	Ν	E
35		н	Н	N	Ν	E
36		7,8(CH <sub>3</sub> ) <sub>2</sub>	н	СН	СН	E
37	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	Н	Н	СН	Ν	E
38	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	Н	н	N	N	E

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		1		Analysis, %			
M.p., °C	Formula	C	н	N	Cl	CH <sub>3</sub> O	
	(Moiecular weight)	Calcd. Found					
	C <sub>15</sub> H <sub>11</sub> ClN <sub>2</sub> O	66.55	4.09	10.35	13.10		
206-207	(270.72)	66.57	4.18	10.31	13.23		
106 107	$\mathrm{C_{16}H_{14}N_{2}O}$	76.78	5.63	11.20			
190-197	(250.30)	76.75	5.73	11.10			
949 940	$\mathrm{C_{17}H_{16}N_{2}O}$	77.25	6.10	10.60			
240-249	(264.33)	77.35	6.19	10.54			
997 990	$C_{15}H_{11}N_3O_2$	67.92	4.18	15.84			
227-228	(265.27)	67.74	4.21	15.86	_	_	
	$C_{15}H_{13}N_3O_2$	67.41	4.90	15.72		11.61	
207-208	(267.29)	67.24	5.02	15.90	-	11.76	
106 107	$\mathrm{C_{14}H_{12}N_4O_2}$	62.68	4.51	20.88		11.57	
190-197	(268.28)	62.79	4.71	21.01	-	11.66	
992 994	$\mathrm{C_{18}H_{18}N_{2}O_{2}}$	73.45	6.16	9.52		10.54	
223-224	(294.35)	73.47	6.30	9.41		10.68	
	CHNO	62 38	5.93	12.84		28 44	
180-181	(327.34)	62.28	5.40	13.07	-	28.45	
206-207	$\mathrm{C_{16}H_{16}N_4O_4}$	58.53	4.91	17.07	_	28.35	
	(328.33)	58.60	4.83	17.02		28.50	

No.	R <sub>1</sub>	$\mathbf{R}_3$	$\mathbf{R_4}$	Q	z	Method
39	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	н	Н	СН	СН	E
40	OCH <sub>3</sub> 	7 Cl	Н	СН	СН	E
41	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	7,8(CH <sub>3</sub> ) <sub>2</sub>	Н	СН	СН	E
42	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	7 NO <sub>2</sub>	Н	СН	СН	E
43	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	Н	-(CH <sub>2</sub> ) <sub>3</sub> -N(CH <sub>3</sub> ) <sub>2</sub>	СН	СН	E
44	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	7 NO <sub>2</sub>	$-(CH_2)_2 - N(C_2H_5)_2$	СН	СН	E
45	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	$7 \mathrm{NO}_2$	-CH <sub>2</sub> -CH <sub>2</sub>	СН	СН	E
46	OCH <sub>3</sub> -OCH <sub>3</sub> OCH <sub>3</sub>	Н	- CH <sub>2</sub>	СН	СН	E

				Analysis, %				
М.р., °С	Formula (Molecular weight)	C	Н	N	Cl	CH <sub>3</sub> O		
	(noteenin wegut)	Calcd. Found						
	$C_{18}H_{18}N_{2}O_{4}$	62.25	5.56	8.58		28.53		
184-185	(326.35)	62.27	5.44	8.50		28.27		
			× 1					
		in a tori						
	C <sub>18</sub> H <sub>17</sub> ClN <sub>9</sub> O <sub>4</sub>	59.92	4.75	7.76	9.82	25.80		
199-200	(360.80)	59.79	4.85	7.87	10.04	25.91		
	CHNO	67.70	6.96	7.00		96 97		
214 - 215	$C_{20}H_{22}N_2O_4$	67.09	6.19	9.17	-	26.27		
	(334.41)	01.02	0.12	0.17		20.09		
	*							
	C1.H1.N.O.	52.23	4.61	11.31	_	25.07		
224 - 225	(371.35)	52.34	4.79	11.42		25.15		
100 100	$C_{23}H_{29}N_3O_4 \cdot 2HCl$	57.03	6.45	8.67	14.64	19.22		
108-109	(484.43)	56.86	6.56	8.73	14.43	19.55		
	C. H. N.O.	(1.07)	( 10	11.01		10.50		
130-131	$U_{24}H_{30}N_4U_6$	61.27	6.42	11.91		19.78		
	(470.55)	01.25	0.40	11.00		19.03		
916 918	$C_{24}H_{30}N_4O_6 \cdot 2HCI$	53.05	5.93	10.31	13.05	17.12		
210-210	(543.45)	53.07	6.02	10.25	12.84	16.98		
1. 1. 1.								
186-188	$C_{25}H_{24}N_4O_6$	63.02	5.07	11.76	-	19.54		
	(476.49)	63.12	4.90	11.60		19.68		
		1						
211-212	$\mathbf{C_{24}H_{23}N_{3}O_{4}}$	69.05	5.55	10.07	_	22.30		
211 212	(417.47)	68.90	5.68	9.96	k y sin he	22.50		
		1	791259159					

### Method D (attempted synthesis of a benzo [1,5] diazepine from a $\beta$ -hydroxyvinylketone)

### 1-[3(4-Methoxyphenyl)-3-oxo-propylideneamino]-2-aminobenzene

To a solution of 13.6 g (0.1 mole) 4,5-dimethyl-o-phenylenediamine in 100 ml xylene there was added 17.8 g (0.1 mole) p-methoxyphenyl- $\beta$ -hydroxyvinylketone [16] and refluxed for 6 hrs. The reaction mixture was then cooled to room temperature. The resulting yellow precipitate was filtered off and washed with xylene to give 20 g (68%) of the product.

A small sample, after recrystallization from xylene for analysis, had m.p. 147–148 °C; IR cm<sup>-1</sup> (KBr): 3320 (s) (NH<sub>2</sub>), 1640 (s) (CO).

If the reaction mixture was refluxed for 12 hrs., the precipitate after recrystallization (from EtOH) was identical in all respects with 5,6-dimethylbenzimidazole, m.p. 202-204 °C. C<sub>9</sub>H<sub>10</sub>N<sub>2</sub> (146.19). Calcd. C 73.95; H 6.86; N 19.17. Found C 73.80; H 6.90; N 18.95%.

 $C_9H_{10}N_2$  (146.19). Calcd. C 73.95; H 6.86; N 19.17. Found C 73.80; H 6.90; N 18.95%. The filtrate was evaporated in vacuum; the *p*-methoxyacetophenone collected had b.p. 125 °C at 5 torr, (lit. [17] b.p. 139 °C at 15 torr.

C<sub>9</sub>H<sub>10</sub>O<sub>2</sub> (150.18). Calcd. C 71.98; H 6.71; CH<sub>3</sub>O 20.66. Found C 72.50; H 6.80; CH<sub>3</sub>O 20.78%.

### Method E (from $\beta$ -ketoesters)

The condensation of o-phenylenediamines with ethyl benzoylacetate was effected in boiling xylene according to previous work [7]. In all cases, however, the conjugated forms, 1,5-dihydro[1,5]benzodiazepine-2-ones were obtained.

### 5,9-Dihydro-6-(3,4,5-trimethoxyphenyl)-8H-pyrimido-[4,5-b][1,4]diazepine-8-one (38)

A solution of 11.0 g (0.1 mole) of 4,5-diaminopyrimidine in 100 ml xylene was refluxed with ethyl 3,4,5-trimethoxybenzoylacetate for 2 hrs. After cooling the solid which separated was collected by filtration and dried to give 26.8 g (82%) of the crude product. Recrystallization from xylene-EtOH yielded cream coloured crystals, m.p. 206—207 °C; IR cm<sup>-1</sup>: 3300—3220 (s) (NH), (CONH), 1650, 1685 (s) (CO).

### 1-[2-(2-Pyridyl)ethyl]-1,5-dihydro-7-nitro-4-(3,4,5-trimethoxyphenyl)-2H-[1,5]benzodiazepine-2-one (52)

### (a) 2-[2-(2,4-Dinitroanilino)ethyl]pyridine

A solution of 20.2 g (0.1 mole) 2,4-dinitrochlorobenzene and 12.2 g (0.1 mole) 2-(2aminoethyl)pyridine in 200 ml EtOH was refluxed for 1 hr. After cooling, 20 ml aqueous (25%) ammonia solution was added to the yellow solution. The yellow solid which precipitated was filtered off, washed with cold water and dried to give 26.5 g (92%) of the product.

A small sample was recrystallized from ethanol; yellow crystals, m.p. 142–143 °C.  $C_{13}H_{12}N_4O_4$  (288.26). Calcd. C 54.17; H 4.19; N 19.44. Found C 54.30; H 4.20; N 19.80%.  $\lambda \max$  (EtOH) (c, 0.5  $\cdot 10^{-4}$  mole) m $\mu$  (log  $\varepsilon$ ); 360 (3.16), 355 (3.28).

### (b) 2-[2-(2-Amino-4-nitroanilino)ethyl]pyridine

A solution of 20.2 g (0.07 mole) of the above dinitroaniline derivative in alcoholic ammonia was treated with hydrogen sulfide gas, keeping the temperature at 40—50 °C for 3 brs., until the spectrum of a small sample had maxima at 265, 410 m $\mu$ , indicating the complete reduction of the ortho-nitro group. The mixture was filtered, and the filtrate evaporated in vacuum. The residual oil was neutralized with hydrochloric acid and extracted with three 100-ml portions of benzene. The benzene solution was evaporated to one sixtieth of its volume.

Ôn cooling a red-brown solid separated which was collected by filtration and dried to give 8 g (35%) of the o-phenylenediamine compound, m.p. 115–116 °C (from benzene).  $C_{13}H_{14}N_4O_2$  (258.19). Calcd. C 60.45; H 5.46; N 21.70. Found C 60.75; H 5.70; N 21.68%.

 $\lambda_{\max}^{13}$  (ÉtŐH) (c, 0.5 · 10<sup>-4</sup> mole) m $\mu$  (log  $\varepsilon$ ): 269 (3.15), 409 (3.08).

(c) 7.7 g (0.03 mole) of the above nitro-o-phenylenediamine and 8.6 g (0.03 mole) ethyl 3,4,5-trimethoxybenzoylacetate was refluxed in 100 ml of xylene.

After cooling, the yellow solid was filtered off and dried to give 10.4 g (73 %) of 52. A sample, recrystallized for analysis, had m.p. 186–188 °C.

### **Tetrahydro** derivatives

## (Table IV)

### Method F (reduction of the dihydro-benzo[1,5]thiazepines and benzo[1,5]diazepines)

### 2.3.4.5-Tetrahydro-4-(4-methoxyphenyl)-[1,5]benzothiazepine (29) from 2,3-dihydro-4-(4-methoxyphenyl)-[1,5]benzothiazepine (19)

### (a) with LiAlH,

A solution of 26.9 g (0.1 mole) of Compound 19 in 300 ml abs. ether was refluxed with 5 g LiAlH, for 24 hrs. The complex was decomposed with water and extracted with a further 300 ml of ether. The ethereal extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residual solid was crystallized from aqueous EtOH to give 21.6 g (80%) of the tetrahydro compound 29. A small sample, recrystallized for analysis, had m.p. 77-78 °C (from EtOH).

### (b) with NaBH,

A solution of 0.1 mole of Compound 19 and 5 g of NaBH<sub>4</sub> in 300 ml abs. EtOH was refluxed for 8 hrs. During that time the yellow colour of the starting material disappeared. After decomposing the complex by adding 100 ml of water, the alcohol was removed in vacuum. The product was extracted with chloroform and the solution dried. The solvent was removed to leave a solid (19.5 g, 72%). A small sample, recrystallized for analysis, had m.p. 77-78 °C.

### (c) Catalytic hydrogenation

2.7 g (0.01 mole) of Compound 19 was hydrogenated in 200 ml of EtOH in the presence of 1 g 10% palladium-on-charcoal catalyst at room temperature for 3 hrs. After removal of the catalyst by filtration, the solution was concentrated, and then diluted with water. The precipitated solid was filtered off and dried to give 2.4 g (90%) of the product, m.p. 77-78 °C (after recrystallization).

### 2,3,4,5-Tetrahydro-7,8-dimethyl-4-phenyl-1H-[1,5]benzodiazepine (49)

A solution of 2.5 g (0.01 mole) 2,3-dihydro-7,8-dimethyl-4-phenyl-1H-[1,5]benzodiazepine (1) was hydrogenated catalytically in the presence of Pd-on-charcoal as above; work-up of the reaction mixture gave 1.9 g (75%) of the product, which was almost white after recrystallization, m.p. 86-88 °C.

### Dihydrochloride

The base was dissolved in acetone and acidified with HCI/EtOH (1:1) to pH = 5; a white solid precipitated. An analytical sample was recrystallized from EtOH-ether to give white crystals of the dihydrochloride, m.p. 196-198 °C.

### Method G (reduction of dihydro[1,5]benzodiazepine-2-ones)

### 2,3,4,5-Dihydro-4-phenyl-7,8-dimethyl-1H-[1,5]benzodiazepine (49)

A suspension of 2.6 g (0.01 mole) 1,5-dihydro-4-phenyl-7,8-dimethyl-2H-[1,5]benzodiazepine-2-one (32) in 100 ml abs. ether was mixed with  $1 \text{ g LiAlH}_4$  suspended in 100 ml abs. ether and the mixture was refluxed for 6 hrs. After decomposition of the complex with water, the ethereal phase was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness in vacuum. The residual material was recrystallized twice from aqueous ethanol to obtain 1.7 g (67%) of the product, m.p. 86-88 °C. The dihydrochloride had m.p. 196-198 °C. An attempt to reduce the above compound (32) with NaBH<sub>4</sub> remained unsuccessful,

because on work-up the starting material was recovered nearly quantitatively.

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No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	Z	Method
47		Н	Н	N	F
48		H	7 Cl	СН	F
49		н	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	F, G
50	<b>F</b>	Н	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	F
51		Н	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	G
52		${ m CH_3}$	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	F
53		н	7,8(CH <sub>3</sub> ) <sub>2</sub>	СН	F

M.p., °C	Formula (Molecular weight)	С	н	N	CI	CH <sup>3</sup> O
	(morecular weight)			Calcd. Found		
95— 98	C <sub>14</sub> H <sub>11</sub> N <sub>3</sub> O (223.28)	75.31 75.22	5.87 5.97	18.82 18.73	_	_
183-184	$\begin{array}{c} {\rm C_{15}H_{15}N_{2}Cl} \\ (258.75) \end{array}$	69.63 69.86	5.84 5.61	10.83 10.56	13.70 13.68	-
103-104	$C_{15}H_{15}CIN_2 \cdot HCl$ (295.22)	61.03 61.14	5.46 5.32	9.49 9.57	24.02 23.96	-
86- 88	$C_{17}H_{20}N_2$ (252.36)	80.91 81.02	7.99 8.05	11.10 11.22	-	-
196-198	$\begin{array}{c} C_{17}H_{20}N_{2}\cdot 2HCl\\ (325.28) \end{array}$	62.77 62.75	6.82 6.98	8.61 8.77	21.80 21.89	
66- 68	C <sub>17</sub> H <sub>19</sub> FN <sub>2</sub> (270.35)	75.53 75.47	7.08 6.90	10.36 10.34	_	-
179-181	$C_{17}H_{19}FN_2 \cdot 2HCl$ (343.28)	59.48 59.50	6.17 6.39	8.16 7.94	20.66 20.45	-
121-123	C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O (282.39)	76.85 76.75	7.85 7.73	9.92 9.86		10.99 11.03
35- 36	C <sub>19</sub> H <sub>24</sub> N <sub>2</sub> O (296.41)	77.00 77.10	8.16 8.02	9.45 9.20	·	10.47 10.29
238-240	C <sub>19</sub> H <sub>24</sub> N <sub>2</sub> O · 2HCl (369.35)	61.79 61.64	7.13 7.27	7.51 7.75	19.15 19.40	8.40 8.48
70- 72	C <sub>19</sub> H <sub>24</sub> N <sub>2</sub> O (296.41)	77.00	8.16 8.22	9.45 9.75		C <sub>2</sub> H <sub>5</sub> O% 15.20 15.35
187-188	$\frac{C_{19}H_{24}N_{2}O \cdot 2HCl}{(369.35)}$	61.79 61.70	7.13 7.17	7.51 7.56	19.15 19.02	12.20 12.36

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				Analysis, %	1	
М.р., °С	Formula (Molecular weight)	с	н	N	CI	CH <sub>3</sub> O
	(molecular weight)			Calcd. Found		
		1				
	C H CIN O	61.09	6.07	0.02	10.16	26 60
58- 59	(349.93)	61.79	5.87	7.81	10.10	26.09
	(340.03)	01.72	5.07	1.01	10.09	20.92
					:	
	CaHacNaO2	70.15	7.65	8.18	_	27.18
65-66	(342.44)	70.16	7.54	8.31		27.44
				-		
208-209	$\mathbf{C_{23}H_{24}N_2O_2}$	76.64	6.71	7.77	- 1	·
200-209	(360.45)	76.48	6.60	7.52		12
						idi
77 70	$C_{21}H_{22}N_2$	83.41	7.33	9.26	_ 11	_
11- 19	(302.42)	83.43	7.43	9.11		
	C <sub>91</sub> H <sub>99</sub> N <sub>9</sub> · 2HCl	67.20	6.44	7.46	18.90	
188-190	(375.34)	67.29	6.21	7.44	19.00	
110 191	$C_{21}H_{22}N_2$	83.41	7.33	9.26	_	-
119-121	(302.42)	83.48	7.48	9.29		
	$\mathbf{C_{21}H_{22}N_2} \cdot \mathbf{2HCl}$	67.20	6.44	7.46	18.90	
181-183	(375.34)	67.35	6.43	7.52	18.69	
	CHN	01.07	7.06	10.06		
50- 52	(279, 40)	01.97	7.90	0.00		-
	(270.40)	01.02	1.90	9.09		
			1.1			-





Table V (continued)

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#### Acetylation of di- and tetrahydrobenzo-[1,5]diazepines

## (Table V)

#### 1,5-Diacetyl-7,8-dimethyl-2-(4-methoxyphenyl)-2,3,4,5-tetrahydro--1H-[1,5]benzodiazepine (63)

A solution of 2.8 g (0.01 mole) 2,3,4,5-tetrahydro-4-(4-methoxyphenyl)-7,8-dimethyl -1H-[1,5] benzodiazepine (51) and 2 g anhydrous NaOAc in 30 ml acetic acid was mixed with 6 ml acetic anhydride and refluxed for 2 hrs. On dilution with water and standing in a refrigerator, white crystals deposited.

The solid was filtered off and recrystallized from aqueous ethanol to give 3.3 g (90%) of the white diacetyl compound, m.p. 187.5 °C.

#### 1-Chloroacetyl-7,8-dimethyl-4-[4-ethoxyphenyl]-2,3-dihydro-1H-[1,5]benzodiazepine (65)

8.8 g (0.03 mole) 2,3-dihydro-4-(4-ethoxyphenyl)-7,8-dimethyl-1H-[1,5]benzodiazepine (7) and 5 g anhydrous NaOAc were dissolved in 60 ml acetic acid and 3 ml chloroacetic anhydride was added; the solution was refluxed for 1 hr. Work-up as above gave 8.6 g (78%) of white crystals, m.p. 138-139 °C (after recrystallization).

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# INFRARED SPECTROSCOPIC STUDIES ON FLAVONOIDS AND MODEL COMPOUNDS, IV

ROTATIONAL ISOMERISM IN 2'- AND 2',6'-SUBSTITUTED CHALCONES

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### Received August 17, 1971

The characteristics of the infrared spectra of 2'- and 2',6'-substituted chalcones were studied by means of various recording techniques. It has been found that the compounds show double absorption in the carbonyl stretching vibration range. On the basis of literature analogues, the phenomenon is attributed to the appearance of S-cis and S-trans rotational isomers. The structural conditions of the occurrence of these rotational isomers have been investigated and a probable arrangement is suggested for the conformation of the compounds on the basis of the experimental results.

Several authors have studied the problem of rotational isomerism in solutions of chalcones carrying different substituents in the 4- and 4'-positions, on the basis of their infrared spectra [1a, b, c, d, e, f, g, h]. According to these investigations, the presence of S-cis (A) and S-trans (B) rotational isomers can be expected in solutions of chalcones, while in the solid state they exist in the S-cis (A) form.



These assumptions are confirmed by the double carbonyl stretching bands appearing in the region  $1630 - 1700 \text{ cm}^{-1}$ ; the band with the higher frequency is assigned to the (A) form. In the conformer equilibrium, isomer (A) is predominant, since it represents an energetically more favourable arrangement [1c, e]. It is evident that the probability of the occurrence of one or the other isomer depends on the space requirement of the atoms or atomic groups located in positions 2' and 6', but this effect of substitution has not been investigated heretofore. The present paper deals with the influence of the space requirement of the substituents on rotational isomerism. Studies on the infrared spectra of 2'-substituted chalcones have been published [2], but no reference to rotational isomers was made in the work.

#### **Results and discussion**

Infrared spectra of the compounds I - VIII (Table I) recorded in the range 1570-1700 cm<sup>-1</sup> by means of various techniques, are shown in Fig. 1; the wavenumber values of the bands observed are summarized in Table II.\*

### Table I

Data of substituted chalcones

No.	R	R <sub>1</sub>	R <sub>2</sub>	Physical constants	Ref.
I	н	Н	н	M.p. 88-89 °C	[3a]
п	-CH <sub>3</sub>	Н	н	B.p. 250 °C/18 torr	[3b]
ш	-CH <sub>2</sub> OCH <sub>3</sub>	Н	н	B.p. 139-140 °C/12.5	[3c]
IV	−C−CH <sub>3</sub> ∥	н	н	torr M.p. 68 °C	[3d]
v	-CH <sub>2</sub> -Ph	н	н	М.р. 85-86 °С	[3e]
VI	-CH <sub>2</sub> -Ph	-OCH <sub>3</sub>	н	M.p. 92-93 °C	see Experimental
VII	-OCH <sub>3</sub>	-0H	н	M.p. 65-66 °C	[3f]
VIII	$-\mathrm{CH}_2-\mathrm{Ph}$	ber	nzo	М.р. 131—133 °С	[3g]



\* It should be noted that the integrated intensity values of the absorptions recorded could not be determined unambiguously because of the large inaccuracy involved in the measurement of the halfwidth values,  $\Delta v_{1/2}$ , resulting from the overlapping of bands (shoulders).



These results clearly show the structural differences in the infrared spectra in the range  $1570 - 1700 \text{ cm}^{-1}$  when recorded in KBr pellets (or liquid film) and in solutions. In the case of solution spectra, some bands are split, new shoulders appear, except for 2'-benzyloxy-6'-OCH<sub>3</sub>- (VI) and 2'-OH-6'-OCH<sub>3</sub>-chalcones (VII). In order to interpret these phenomena, it can be sup-



posed on the basis of literature analogues [1] that in the case of 2'-substituted compounds S-cis and S-trans rotational isomers may exist, thus the band of higher frequency (1640 - 1680 cm<sup>-1</sup>) is due to the vC=0 vibration of the S-cis form; the band appearing between 1620 and 1650 cm<sup>-1</sup> often forms a 'shoulder' and its intensity is lower than that of the former; this band can be assigned to the carbonyl stretching vibration of the S-trans form.

The broad band of high intensity found between 1580 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> can be identified as the stretching vibration of the conjugated C=C bond. It is very probable that this band overlaps the bands of the skeletal vibration types 8a and 8b mono- and 1,2-disubstituted aromatic rings. The sharp band appearing in the 1570–1585 cm<sup>-1</sup> range can be assigned to the 8b skeletal vibration of the monosubstituted ring B [4].

The presence of conformers is verified by the experience that, on changing the  $CCl_4$  solvent to  $CHCl_3$ , the  $\nu C=O$  bands assigned to the S-*cis* form undergo, in general, a smaller shift than the corresponding bands of the S-*trans* forms [5].

The compounds examined contained an -OR group (R=H, Me, Ac, benzyl) in position 2'. The position of this -OR group with respect to the carbonyl group, *i.e.*, the appearance of conformers (C) and (D) was the subject of our investigation.\*

<sup>\*</sup> We refer to our current NMR studies, according to which the protons of the -OR group give rise to one sharp singlet between  $\delta 3.8$  and 5.5 ppm at room temperature. A detailed investigation is in progress.

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These two forms cannot be equivalent, since free rotation about the bond between the aromatic ring and the carbonyl group is prevented by conjugation. (Rotation about this bond has been investigated in benzaldehydes and acetophenones [6a, b, c, d, e], and the results also indicated the absence of free rotation. This fact is further verified by our quantum mechanical calculations on chalcones [7].) If these compounds existed in form (C), only the S-*cis* conformer (E) would appear in solution and one single  $\nu C=0$  band would be found, since the development of the S-*trans* form (F) is sterically hindered by the 2'-OR group.



If, however, the presence of form (D) is supposed, no steric hindrance occurs and the S-*trans* form can develop. The conformer equilibrium ( $G \rightleftharpoons H$ ) is characterized by double  $\nu C = O$  absorption (Fig. 1). This assumption is in accordance with the experimental findings.



It is supported by the fact that the 2'-OH derivative certainly exists in the (D) form also in crystalline state, since the -OH and C=O groups are involved in a very strong resonance chelate [2]. The infrared spectra of 2'-substituted chalcones were investigated by SABATA et al. [2], who showed that the occurrence of resonance form (I) should be considered for these compounds.



(Our quantum chemical calculations  $(\delta + \pi)$ , to be published shortly verified the presence of a positive net charge at the ethereal oxygen atom; this can also be deduced from simple resonance considerations.)

This form is stabilized by coulombic interaction. According to our studies, its stability depends on the nature of the R group; in the case of R = H. Me. it is very stable, while in the presence of acetyl, benzyl, etc., as these groups are weaker electron donors, the polarity of the C=O group decreases, i.e., the  $\nu C = 0$  frequency increases. This is corroborated by the data given in Table II. Recent infrared spectroscopic studies on benzophenones also confirmed the existence of hindered rotation [7]. Latest results regarding hindered rotation in compounds of chalcone type have been reported by MEUNIER. and FOURNARI [9]. Other data of similar character can be found in the literature [1h, 10, 11]. In the case of 2'-benzyloxy-6'-methoxy- (VI) and 2'-methoxy-6'-hydroxychalcone (VII) (Fig. 1, Table II), no change was observed in the structure of the spectrum in the C=O stretching vibration range; in both compounds a band appeared at about 1630 cm<sup>-1</sup>, however, this can also be found in the spectrum recorded in KBr pellets, thus it can be assigned to the skeletal vibration of the vicinally trisubstituted aromatic ring [12]. In these cases no rotational isomers can appear. These compounds exist only in the S-cis (J) conformation both in solid state and in solution.



According to the investigations, it is probable that in the 2'-benzyloxy-6'-methoxy compound (J) R = benzyloxy and  $R_1 = CH_3$ , while in the 2'-methoxy-6'-hydroxy compound (J) the infrared spectrum surely confirms that  $R = CH_3$  and  $R_1 = H$ . (This is supported by the solution spectra, too.)

The carbonyl stretching frequencies observed in these compounds (Table II) indicate that the conjugation existing between the carbonyl group and the aromatic ring does not diminish on introducing a new substituent because of its occasional steric effect. If the coplanarity between the carbonyl group and



# Table II

Characteristic infrared frequency values of 2'- and 2',6'-substituted chalcones in the range 1570-1700 cm<sup>-1</sup>

No	P	KBr pellets (cm <sup>-1</sup> )													
140.	R	n <sub>1</sub>	R <sub>2</sub>	*liquid film		CCl <sub>4</sub> cm <sup>-1</sup>			CHCl <sub>3</sub> cm <sup>-1</sup>						
I	H	H	H	1642;		1583;	1570	1642;	1619;	1587		1642;	1619;	1585	
п	CH <sub>3</sub>	н	н	1660;	1647sh;	1611;	1580	1663;	1648sh;	1606;	1584	1657;	1640sh;	1603;	1580
III	CH <sub>2</sub> OCH <sub>3</sub>	н	н	1664;	1650sh;	1613;	1582	1665;	1643sh;	1604;	1578	1660;	1641sh;	1600;	1577
IV	COCH <sub>3</sub>	н	Н	1670;	1639;	1609;	1580	1672;	1650;	1608;	1578	1667;	1642;	1604;	1575
V	$CH_2C_6H_5$	н	н	1657;		1610;	1590	1660;	1643sh;	1604;	1576	1655;	1640;	1601;	1575
VI	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	OCH <sub>3</sub>	H	1662;		1631;	1598	1662;	1630;	1610sh;	1598	1650;	1630sh;	1597	
VII	OCH <sub>3</sub>	ОН	н	1640;	1630;	1593;	1578	1640;	1626;	1585		1638;	1623sh;	1580	
VIII	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	ber	izo	1665;	1625;	1600;	1578	1655;	1642;	1605;	1580	1642;	1630;	1595;	1575

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the aromatic ring decreased appreciably, the carbonyl stretching frequency should increase considerably ( $\sim 1690 \text{ cm}^{-1}$ ), as observed in the corresponding acetophenones [10]. This, however, was not observed in our work.

NMR studies at various temperatures are in progress on the conformational problems mentioned above (equivalence of forms (C) and (D)). These seem to support the results of the infrared spectroscopic investigations.

# Experimental

The infrared spectra were recorded with a Zeiss UR-10 spectrophotometer in KBr (Uvasol Merck) pellets, in liquid films and in CCl<sub>4</sub> and CHCl<sub>3</sub> (BDĤ) solutions. The accuracy of the measurement was  $\pm 1$  cm<sup>-1</sup>. Concentrations of 0.2–0.05 M were used; the layer thickness was 0.5-0.05 mm.

The compounds listed in Table I were used in the investigations. These were synthesized partly according to literature prescriptions and some of them were prepared first by us.

#### 2'-benzyloxy-6'-methoxychalcone (VI)

2'-Hydroxy-6'-methoxychalcone (VII) (4 g) was refluxed benzyl chloride (3.25 cm<sup>3</sup>; 1.1 mole) in the presence of ignited  $K_2CO_3(12)$  g in absolute acetone (100 cm<sup>3</sup>) for 24 hrs. After filtering off the salt, the solvent was evaporated in vacuum and the residue recrystallized from ethanol to obtain 3.8 g (73.5%) of the product, m.p. 92-93 °C.

C23H2003 (344.39). Calcd. C 80.25; H 5.84. Found C 80.30; H 5.75%.

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# STEROIDS, XXI

# COMPARATIVE KINETIC STUDIES ON THE OXIME FORMATION REACTION OF STEROID KETONES\*

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Under the conditions applied in the experiments, the kinetic and thermodynamic parameters of oxime formation from steroid ketones and other carbonyl compounds are comparable and can easily be followed.

The investigations have shown that oxime formation reactions are described kinetically most appropriately by a rate equation of second order.

The kinetic and thermodynamic data allow conclusions as regards the stereochemical, thermodynamic and reactivity factors involved in the oxime formation of various ketones.

The carbonyl groups of natural steroid ketones play an extremely important part in the biological activity of the compounds. In several cases, the specific hormone action depends on the location of the carbonyl groups within the molecule. The reactivity of the carbonyl group of substances having similar structures but differing in their hormone action may be influenced by the nature of the other substituents present in their relative positions with respect to the carbonyl group in the steroid skeleton. If the oxygen atom of the carbonyl group is substituted by another atom or radical in steroid hormones, in addition to a change in the hormone action of the molecule, other properties of the steroids will also be altered [1].

HAMMET [2] and JENCKS [3, 4] have dealt in detail with the kinetics of the oxime- and semicarbazone formation of aldehydes and ketones in aqueous medium, and they found a strong pH dependence for these reactions. The reaction steps are the following:



$$\begin{array}{|c|c|} & OH \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & &$$

(in the present case, R=OH).

\* Part of the lecture held at the Conference of the Hungarian Chemical Society, Debrecen, August 30—September 1, 1971.

The process leads through an intermediate, with the subsequent formation of the end-product. The second step, formation of the oxime, *i.e.*, the elimination of a water molecule, is the slower one, therefore, the overall reaction rate will be determined by  $k_2$ , particularly when the pH of the reaction is about neutral.

Oxime formation from hydroxybenzaldehydes in non-aqueous medium was studied by KNOPPE and EMANUEL [5]. They found the rate of formation of the intermediate to be very rapid as compared with the other steps. According to their statement, the overall reaction is second order. Further on, the authors studied the influence of the formation of hydrogen bridges on the reaction mentioned above.

In the literature, only few data are available on the kinetics of the oxime formation of steroid ketones.

Titrimetric following of the formation of steroid ketoximes has been utilized by Göröc [6] for the quantitative determination of steroids containing isolated keto groups.

RALLS [7] suggested the existence of isomeric syn and anti modifications of cholest-4-ene-3-one oxime on the basis of the bromine addition and different refractive indices of two crystalline forms (A and B modifications) of the above oxime isolated from different solvents and having different melting points.

DECOMBE et al. [8] compared the rates of the oximation of cholestane-3-, -4-, -5-, -6- and -7-one; the reaction was followed by titration, and the  $N_2$ liberated from the nitrogen of the oxime group by means of potassium permanganate was also measured quantitatively in an ureometer. The results were used for drawing conclusions on the conditions of the formation of isomeric oximes.

In our experiments, the reactivities and activation parameters of the oximation reactions of different steroid ketones were compared with one another and with those of non-steroid ketones.

# Experimental

When hydroxylammonium chloride is used without a buffer, the pH undergoes a change in the course of the reaction; therefore, hydroxylammonium salicylate was used as the oximating agent.

Though oxime formation occurs rather slowly in chloroform, yet this solvent was found to be the most suitable, because steroids are very well soluble in  $CHCl_3$  or in a 2 : 1 mixture of chloroform and methanol used in our experiments [9].

The reaction was carried out in a three-necked round-bottomed flask equipped with a stirrer and a sampling device designed for this purpose. The reaction vessel was placed into an ultrathermostat. First, the ketone was dissolved in the solvent mixture mentioned and the reaction was started by the addition of hydroxylammonium salicylate. Samples were taken periodically from the reaction mixture, and the oxime formation reaction was stopped by cooling the sample in ice. The actual hydroxylammonium salicylate concentration was determined by titration with 0.005 N HCl (prepared in a 1 : 1 mixture of 1,2-propanediol and chloroform) in the presence of Dimethyl Yellow Methylene Blue mixed indicator [9]. The reaction products were identified by means of thin-layer chromatography. The end-product gave only the spot of the oxime [10].

In the course of the investigation, the concentration of the ketone was varied between  $4-20 \times 10^{-3}$  and  $10^{-4}$  mole/l in order to determine the optimum concentration ratio, while the concentration of hydroxylammonium salicylate was maintained at 0.005 mole/l.

The results were well reproducible.

In the kinetic measurements, the temperature was varied mainly between 20 °C and 50°C. The steroid ketones examined were obtained from the Gedeon Richter Works (Budapest) and purified by us, or prepared from starting materials supplied by this company, according to literature methods or those developed by us [11].

The non-steroid ketones examined were also commercial products (Aldrich, USA), with physical and chemical characteristics reported in the literature.

# **Results and discussion**

On plotting the actual hydroxylamine concentration on the ordinate and the reaction time on the abscissa, the curve shown in Fig. 1 was obtained for estrone.

In Fig. 2, one of the sides of the integrated form  $\frac{1}{a-b}\left[\ln\frac{b}{a}\frac{(a-x)}{(b-x)}\right]$  of the second-order rate equation is shown on the ordinate and the reaction time (sec) is given on the abscissa. This representation gives a straight line for estrone as shown in the Figure.

Data processing was carried out with a MINSK-22 computer.



Fig 2

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Fig. 3 shows the logarithm of the rate constants as a function of the reciprocal temperature; the activation enthalpy  $(\Delta H^{\ddagger})$  and activation entropy  $(\Delta S^{\ddagger})$  were calculated from the slope of the curves and from the intercept on the axis, respectively, according to the following equation:

$$k = \frac{kT}{h} e^{\frac{S^{\ddagger}}{R}} \cdot e^{-\frac{H^{\ddagger}}{RT}}$$

(In the calculations the log kT/h = 12.828 value (50 °C) was used.)

The results obtained for estrone and its derivatives are summarized in Table I.

	k×10 <sup>2</sup> ; 45 °C
Estrone	1.53
Estrone-3-methyl ether	3.09
Estrone-3-isopropyl ether	3.37
Estrone-3-benzyl ether	3.58
Estrone-3-cyclopentyl ether	3.68
Estrone-3-acetate	3.583

Table I

In Table I, the reaction rate constants of estrone measured at  $45 \,^{\circ}\text{C}$  are compared with those of estrone derivatives measured at similar temperature.

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In this series, as shown by the Table, estrone is the least reactive; the methyl, isopropyl, benzyl and cyclopentyl ether derivatives show increasing reactivity; that of the acetate is nearly equal to the reactivity of the benzyl ether.

It can be stated on the basis of the comparative data given in Table I that substitution of the hydrogen atom in the phenolic hydrogen group at C-3 with different alkyl, cycloalkyl or acyl groups alters the nucleophilic character of the carbonyl oxygen at C-17, which naturally promotes the first step of the oximation reaction, *i.e.*, the binding of the proton.

Let us now examine the data in Table II, which show the activation enthalpy and entropy values of various steroid ketones and some model carbonyl compounds.

		1
	∆H <sup>‡</sup> cal/mole	⊿S <sup>‡</sup> cal/mole×degree
Estrone	7.77	- 9.318
Testosterone	9.87	-33.63
Testosterone-17-beta- propionate	12.03	-29.13
Nortestosterone	13.71	-20.90
Cholest-4-ene-3-one	6.31	-47.13
Cyclohex-2-ene-1-one	6.07	-36.40
Cyclopentanone	14.63	- 7.08
Cyclohexanone	the reactio to allow	n is too rapid evaluation
Cycloheptanone	9.15	-28.57
Cyclooctanone	21.76	12.80
alfa-Tetralone	7.18	-35.62
beta-Tetralone	5.53	-41.16

**Table II** 

On comparing the reactivity of estrone with that of testosterone or testosterone propionate (the latter two compounds are known to exhibit male sexual hormone action, and in these compounds the keto group is located at C-3 being in conjugation with a double bond), Table II shows a striking difference in reactivity, the comparison being unfavourable for estrone.

The enthalpy of the oxime formation of testosterone is also higher by about 2 cal/mole.

It is interesting to examine the thermodynamic values of the oximation of cholest-4-ene-3-one which contains a similar ring A; in this case it is probably the long alkyl side-chain attached to C-17 which influences the oxime formation, thus the activation enthalpy of the reaction is even lower than that of estrone. The high  $\Delta H^{\ddagger}$  value of testosterone propionate is in accordance with the above facts. The value of the activation enthalpy is highest in the case of nortestosterone, probably because the electron donating effect of the methyl group at C-10 is absent.

In order to get a deeper understanding of the problems revealed by our experiments, the reactivity of cyclohexanone was also examined; the reaction rates obtained were the highest in this case, the rate constant being higher than 3. (This reaction is the fastest among the carbonyl compounds investigated.)

The activation enthalpy of cycloheptanone used for comparison was 9.15 cal. and that of cyclooctanone was 21.76 cal.; this was the second highest value among the alicyclic ketones. The activation enthalpy of cyclohex-2-ene-1-one was 6.07 cal., close to that of cholest-4-ene-3-one. On the other hand, the  $\Delta H^{\ddagger}$  value of cyclopentanone was 14.63 cal., the value of its activation enthalpy lying between those of cycloheptanone and cyclooctanone. It has been supposed that the thermodynamic values measured in model compounds containing an aromatic ring attached to the cyclopentane or cyclohexane skeleton will be close to those of carbonyl compounds comprising a steroid structure. Therefore, the reaction kinetics parameters of the oximation reaction of tetralones were studied.

The activation enthalpy value of alfa-tetralone was 7.18 cal/mole, and it can easily be measured; the  $\Delta H^{\ddagger}$  value of beta-tetralone containing an isolated carbonyl group was 5.53. From this point of view, the values measured seem to be most similar to those of conjugated ketones.

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# AROMATIC SULPHENYL CHLORIDES, VI

REACTION OF SULPHENYL CHLORIDES WITH C-ARYLOXY-N-ARYLIMINOMETHANE-S-OXIDES

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- Received December 13, 1971

The reactions of various substituted C-aryloxy-N-aryliminomethane-S-oxides and of the sulphenic acid tautomers of these oxides with *p*-toluenesulphenyl chloride were studied. It was found that the sulphenyl halides react with one of the tautomeric forms of sulphenic acid under the elimination of hydrochloric acid, to afford the corresponding S-*p*-toluene-thiosulphinic acid ester. The investigations appear to confirm the conditions of thiosulphinate formation starting from sulphenyl chlorides. The structures of the initial substances and the reaction products were proved by the IR spectra.

WALTER and BODE [labc] studied the oxidation of N-arylthiocarbamic acid O-aryl esters (I) prepared by them earlier. It was found that this oxidation affords a stable sulphur oxide (II) only if the compounds to be oxidized carry various ortho substituents in their O-aryl ring, while alkyl substituents are present in the 2,6-positions in the N-aryl ring:



In the opinion of the mentioned authors, the SO group is sterically fixed by these substituents (or by the substitutions in the mentioned positions), as they induce the formation of an intramolecular hydrogen bridge, which acts as a hindrance to intermolecular association. Further, it was observed by these authors [1c] that in compounds where substituent  $R_2$  is a phenyl group (IIa), a tautomeric equilibrium exists between the sulphur oxide and its protonated form, iminomethanesulphenic acid (IIIa). This presumption was supported by infrared spectral investigations proving the simultaneous presence of  $\nu S \rightarrow 0$  and  $\nu C = N$  bands.



where  $a: R_1 = H; R_2 = C_6H_5; R_3 = R_4 = CH_3$  $b: R_1 = R_2 = CH_3; R_3 = R_4 = H$  $c: R_1 = H; R_2 = R_3 = R_4 = CH_3$ 

Thione-thiol tautomerism is also possible in compounds I. This was proved in our earlier investigations [2] by the observation that, e.g., in their reaction with p-toluenesulphenyl chloride the corresponding N-aryl-isothio-carbamic acid-S-(p-toluenesulphenyl)-O-phenyl esters were formed.

In contrast to the unstable sulphenic acids described thus far in the literature, the sulphur oxide in its tautomeric form (iminomethanesulphenic acid) prepared by WALTER and BODE [1c] proved to be an easily available and rather stable compound.

VINKLER and one of us (F. KLIVÉNYI) [3, 4] studied earlier the hydrolysis of aromatic sulphenyl chlorides (IV) where non-isolable sulphenic acid (V) is formed as an intermediate. It has been presumed that the first stable product of this hydrolysis, the thiosulphinate (VI) is obtained, according to the equation below, from two tautomers of sulphenic acid of amphoteric character, by the elimination of water.

$$\begin{array}{c|c} \operatorname{Ar}-S-\operatorname{Cl} \xrightarrow{H_2O} & [\operatorname{Ar}-S-\operatorname{OH} \rightleftharpoons \operatorname{Ar}-S-\operatorname{H}] \xrightarrow{-H_2O} & \operatorname{Ar}-S-S-\operatorname{Ar} \\ & & & & \\ & & & \\$$

However, the formation of the thiosulphinate may also be interpreted in a way that one of the tautomers of sulphenic acid (Va or Vb) reacts with still unreacted sulphenyl chloride to give thiosulphinate. The iminomethanesulphenic acids appeared to be suitable model compounds for the elucidation of this problem. Namely, if the reaction of compound IIIa with p-toluene sulphenyl



chloride affords, e.g., a mixed thiosulphinate, then the process shown below seems probable.

The structures of the initial compounds (II) and of the sulphenylated products (VII) were studied by infrared spectral investigations.

The broad band between 2700 and 2400 cm<sup>-1</sup> appearing in the vicinity of the vNH band in the infrared spectrum of compound **Ha** (Fig. 1), further



the simultaneous presence of bands vC=N and  $vC=S \rightarrow O$  (see Table I) indicate the existence of a tautomeric equilibrium in this compound between **IIa** and **IIIa**, even in the solid state. The infrared spectra of compounds **IIb** and **IIc** (e.g., Fig. 2) have the bands vNH and  $\beta NH$  characteristic of thioamides, and the band  $vC=S \rightarrow O$  also appears (see Table I). Thus, compounds **IIb** and **IIc** may be considered to have a uniform sulphoxide structure, in contrast to the preceding compound.



On subjecting compounds IIa, IIb and IIc to sulphenylation, the thiosulphinate-type compounds of structure VIIa, VIIb and VIIc are obtained. Consequently, the derivatives VII of compounds IIb and IIc may be derived from the tautomeric forms IIIb and IIIc. According to this observation, oxidation may give stable sulphur oxides also from such N-aryl-thiocarbamic

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acid O-aryl esters which differ from the structures defined by WALTER and BODE [1c].

As an evidence of the presumed structure, the bands vC=N,  $vS-S \rightarrow O$ and the band  $\gamma C_{Ar}H$  characteristic of *p*-disubstitution appear in the spectra of compounds **VIIa**, **VIIb** and **VIIc** (e.g., Fig. 3, 4), whereas the bands vNH and  $\beta NH$  of the initial compounds are absent, and so is the band of 950 cm<sup>-1</sup> of compounds **IIb** and **IIc**, which may be assigned to the vibration  $vC=S \rightarrow O$ (see Table I).



As a result of the present investigations it may be stated that sulphenic acids are in fact intermediates in the production of thiosulphinates from sulphenyl chlorides, and that thiosulphinates are not necessarily formed by the condensation of two tautomeric sulphenic acids of amphoteric character.

The experiments also confirm our earlier observation [2] that in the sulphenylation reaction of thiocarbamic acid derivatives the electrophilic substitution occurs always on the sulphur instead of the nitrogen atom.





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$\mathrm{cm}^{-1}$	IIa Fig. 1	IIb Fig. 2	Пс	<b>VIIa</b> Fig. 3	VIIb Fig.4	VIIc
νNH	3050-3000	3200 - 2700	3180-2900	_		
ν(S)0 H	2700-2400	-	-	-	-	-
βNH		1550	1490	-	-	_
$\nu$ -S-S $\rightarrow 0$	-	-	-	1105 1090	1090	1080
$\nu C = S \rightarrow O$	910	950	950	_	-	-
$v_{s}C_{Ar} - O - C$	1200 - 1160	1160 - 1100	1140 - 1110	1160 - 1140	$1170\!-\!1120$	1160-1110
$\nu C = N$	1640-1610		-	1640	1650	1640
$\gamma C_{Ar} H$ (p-disubst.)	-	_	-	810	820	780
$\gamma C_{Ar} H$ (o-disubst.)	750	-	740	740		740
$\gamma C_{Ar} H$ (1,2,3-trisubst.)	770	770 750	770	770	780 770	760 .
$\gamma C_{Ar}H, \gamma C_{Ar}C_{Ar}$ (monosubst.)	_	690	-		700	

Characteristic data of the infrared spectra of compounds II and VII recorded in KBr pellets (cm<sup>-1</sup>)

# Experimental

#### (Melting points are uncorrected)

Infrared spectra were recorded in potassium bromide pellets, with a Perkin-Elmer-457 and a Spectromom Type 2000 spectrophotometer.

# C-(2-Phenylphenoxy)-N-(2,6-dimethylphenyl) iminomethane-sulphinic acid-S-p. toluene-thiol ester (VIIa)

Anhydrous pyridine (0.6 g; 0.008 mole) was added to a solution of 2.8 g (0.008 mole) C-(2-phenylphenoxy)-N-2,6-dimethylphenyliminomethanesulphenic acid\* (IIIa) (m.p. 118—120 °C, from a mixture of benzene and petroleum ether) in 20 ml anhydrous ether, then a solution of 1.2 g (0.008 mole) p-toluenesulphenyl chloride in ether was added dropwise, with stirring. When the red colour of the solution disappeared, the precipitated pyridine hydrochloride was filtered off, and the ethereal filtrate was washed with water until neutral, and dried. The residue obtained on evaporation of the solvent was a yellow, solidifying oil (1.9 g; 50.3%).

Recrystallization from petroleum ether containing some benzene gave pale yellow needles, m.p. 116-118 °C.

C<sub>28</sub>H<sub>25</sub>NO<sub>2</sub>S<sub>2</sub> (471.645). Calcd C 71.31; H 5.34; N 2.97. Found C 70.74; H 5.65; N 2.83%.

#### C-(2,6-Dimethylphenoxy)-N-(phenyl) iminomethane-sulphinic acid-S-p. toluene-thiol ester (VIIb)

A suspension of 2.21 g (0.008 mole) C-(2,6-dimethylphenoxy)-N-(phenyl)-aminomethane-S-oxide (IIb) (m.p. 123—124 °C, from a mixture of benzene and petroleum ether) in 40 ml ether was allowed to react in the presence of 0.60 g (0.008 mole) pyridine with 1.30 g (0.008 mole) *p*-toluenesulphenyl chloride as described above for VIIa and processed in the same way. After evaporation of the solvent, the residue was 1.05 g (33.2%). When recrystallized from a 1 : 2 mixture of benzene and petroleum ether, yellow prisms of m.p. 119—121 °C were obtained.

C22H21NO2S2 (395.56). Calcd C 66.79; H 5.35; N 3.54. Found C 66.72; H 5.78; N 3.30%.

# C-(2-Methylphenoxy)-N-(2,6-dimethylphenyl) iminomethane-sulphinic acid-S-p. toluene-thiol ester (VIIc)

A solution of 2.90 g (0.01 mole) C-(2-methylphenoxy)-N-(2,6-dimethylphenyl)-aminomethane-S-oxide (**Hc**) (m.p. 110—112 °C, from petroleum ether) in 50 ml ether was allowed to react, in the presence of 0.80 g (0.01 mole) pyridine, with 1.60 g (0.01 mole) p-toluenesulphenyl chloride at -10 °C as described for **VHa**. The residue left after evaporation of the solvent was a red-coloured oil. It was subjected to empirical chromatography on a silica gel column, using petroleum ether as the eluting agent. Evaporation of the solvent left a residue of 0.75 g (18.3%). Recrystallization from a 1:1 mixture of benzene and petroleum ether gave pale yellow prisms, m.p. 113—114 °C.

C23H23NO2S2 (409.57). Calcd C 67.46; H 5.66; N 3.42. Found C 68.03; H 5.73; N 3.37%.

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\* The sulphenic acid (IIIa) and sulphur oxides (IIb and IIc) used as initial compounds were prepared by the method of WALTER and BODE [1c], by oxidizing the appropriately substituted N-aryl-thiocarbamic acid O-aryl esters with hydrogen peroxide.

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# FORMATION OF HYDANTOIN IN THE ALKALINE HYDROLYSIS OF METHYL N-CARBOBENZOXY-4,6-O-BENZYLIDENE-D-GLUCOSAMINOYLGLYCINATE

## (SHORT COMMUNICATION)

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In the course of our research work on the preparation of peptides containing D-glucosaminic acid as the amino acid component, the preparation of N-carbobenzoxy-4,6-O-benzylidene-D-glucosaminoylglycine was planned. N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminic acid ethylester(I), described previously [1] was converted into its hydrazide (II) and this was allowed to react with methyl glycinate according to the method of azide coupling, resulting in methyl N-carbobenzoxy-4,6-O-benzylidine-D-glucosaminoylglycinate (III):



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The hydrolysis of the ester (III) was effected with 1 N sodium hydroxide solution, the substance being suspended in a mixture of acetone-water (see Experimental). The progress of the reaction was checked by thin-layer chromatographic examination of samples withdrawn periodically. The amount of the starting material was found to decrease gradually for about one hour; no change was observed in the next 2-hour period. The substance obtained after the usual processing of the reaction mixture was poorly soluble in ethyl acetate and very well soluble in water; at pH 4, its solubility was about ten times higher in water than in ethyl acetate. M thylene chloride, chloroform and ether dissolved the substance even worse than ethyl acetate. These solubility conditions rendered its recovery from the aqueous hydrolyzate difficult.



Fig. 1. IR spectrum of 5-(2,4-O-benzylidene-1,2,3,4-tetrahydroxybutyl)-hydantoin-3-acetic acid (KBr)

Since continuous extraction could not be used because of the high sensitivity of the protective groups to acids, repeated extraction was applied and the degree of extraction was checked by means of thin-layer chromatography. The combined ethyl acetate extract was evaporated to dryness in vacuum and the product was crystallized from ethanol. The products obtained from parallel experiments melted at 172 - 175 °C, 178 - 181 °C and at 186 °C, with decomposition.

In the infrared spectra (Fig. 1), the broad band appearing in the 2400 – 3600 cm<sup>-1</sup> wavenumber region indicated the presence of a carboxylic group. The  $v_{as}$  C – C – O band and the bands characteristic of monosubstituted aromatic rings are absent at 1245 cm<sup>-1</sup> and at 700 cm<sup>-1</sup> and 745 cm<sup>-1</sup>, respectively. The strong, broad band appearing at 1755/1745 cm<sup>-1</sup> probably contains the rCO band of the carboxylic acid group, in addition to the rCO band; further a new band appears at 1670 cm<sup>-1</sup>. These facts and literature data allow the conclusion that the carbobenzoxy group is split off under the conditions of alkaline hydrolysis; only the hydantoin derivative can be isolated from the reaction mixture in pure state.

This reaction has been known for a long time [2a, b, c] and it takes place mainly when glycine is present next to the amino acid carrying the carbobenzoxy group.

On the basis of the above facts and considering the infrared spectrum and the analysis data, it can be stated that the alkaline hydrolysis gave 5-(2,4-O-benzylidene-1,2,3,4-tetrahydroxybutyl)-hydantoin-3-acetic acid (that is, 5-(2,4-O-benzylidene-1,2,3,4-tetrahydroxybutyl)-2,4-dioxo-3-imidazolidine acid) (**IV**) instead of the expected product.



# Experimental

Melting points are uncorrected. The infrared spectra were recorded on a Zeiss spectrophotometer Model UR 10 (KBr). The  $R_f$  values were determined using the ascending technique of thin-layer chromatography in the following solvents: (1) CHCl<sub>3</sub>: MeOH = 9 : 1; (2) BuOH : : AcOH :  $H_2O = 80 : 20 : 5$ ; (3) BuOH : AcOH : AcCH<sub>3</sub> = 80 : 20 : 20. For the detection of the spots ninhydrin and chlorotoluidine was used, respectively.

#### N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminic acid ethyl ester (I)

4,6-O-Benzylidene-D-glucosamine ethyl ester hydrochloride (27 g; 0.077 mole) [1] was dissolved in water (390 ml) at room temperature and chloroform (614 ml) and magnesium oxide (5.6 g) were added to the solution. The suspension was cooled to 2 °C and carbobenzoxy chloride (24.2 g; 0.142 mole) was added to it dropwise under vigorous stirring. The mixture was agitated further for 5 hrs. at 2 °C. The excess of acid chloride was then decomposed with pyridine 5.6 ml, and the pH was adjusted to 3 with 5 N HCl solution. After separation, the chloroform phase was washed until free from acid, dried and evaporated to dryness in vacuum to obtain 29.07 g (84.3%) of the product, m.p. 145°;  $R_I^I = 0.98$ .

#### N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminic acid hydrazide (II)

N-Carbobenzoxy-4,6-O-benzylidene-D-glycosaminic acid ethyl ester (2.22 g; 0.005 mole) was dissolved in 20 ml of hot absolute ethanol and of 98% hydrazine hydrate (0.65 g; 0.013 mole) was added to it. The solution was refluxed for 1 hr then allowed to cool to room temperature. The crystal needles which separated on standing for 24 hrs were filtered off and washed with some cold (-10 °C) absolute ethanol. After recrystallization from acetonitrile (200 parts) the pure hydrazide was obtained in 78% yield, m.p. 195–196 °C;  $R_{\rm f}^1 = 0.85$ .  $C_{21}H_{25}N_{3}O$ , (431.449). Calcd C 58.44; H 5.84; N 9.74. Found C 58.22; H 6.07; N 9.50%.

IR: Amide I (Z) 1705; Amide I (hydrazide) 1760; Amide II 1520 cm<sup>-1</sup>.

#### M ethyl N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminoyl glycinate (III)

N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminic acid hydrazide (5 g; 0.011 mole) was dissolved in absolute dimethylformamide (10 ml) at room temperature and the solution was cooled to -15 °C. First 20% hydrochloric acid (6.9 ml; 0.04 mole) was added to it at maximum -10 °C temperature, followed by a solution of sodium nitrite (1.07 g; 0.0146 mole) in water (7.3 ml), added dropwise; the sodium nitrite solution was then rinsed in with 4 ml of dimethylformamide. The mixture was stirred for 5 min more at -10 °C and cooled to -20 °C in 2 min.

At the same time, glycine methyl ester hydrochloride (4.58 g; 0.0365 mole) was dissolved in dimethylformamide (66 ml), cooled to - 20 °C and triethylamine (15.4 g; 0.152 mole) was added dropwise to the solution (FH 8). The azide solution prepared above and cooled to -20 °C was added to this solution by drops with vigorous stirring; the temperature must not rise above -10 °C during the procedure and the pH of the solution should not become lower than 8. Undesired acidification was prevented by the addition of triethylamine. The mixture was stirred for 1 hr at -10 °C, then it was kept at 0 °C for 22 hrs. After this the dimethylformamide was evaporated on a water bath of maximum 35 °C at a pressure of 0.6 torr, and the solid residue (m.p. 123-126 °C) was dissolved in a mixture of 1000 ml of ethyl acetate and 1000 ml of 20% sodium chloride solution at 0 °C. The aqueous phase was extracted twice with ethyl acetate (50 ml each) and the combined organic phase was washed with 20% sodium chloride solution ( $6 \times 70$  ml) at 0 °C (until the aqueous phase showed negative ninhydride reaction). The ethyl acetate solution was dried over anhydrous sodium sulfate and evaporated to dryness in vacuum at 20 °C to leave 5.8 g of the product, m.p. 175-179 °C. The crude product was dissolved in methanol (30 parts) and precipitated with a 1:1 mixture of ether and petrolether (15 parts), then it was crystallized from ethyl acetate (80 parts). Thus 3.4 g (60.0%) of III was obtained, m.p. 188 °C.  $R_{f}^2 = 0.90$ . C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>9</sub> (488.506). Calcd. C 59.01; H 5.78; N 5.74. Found C 58.92; H 5.58; N 5.64%.

IR: vCO (ester) 1745, Amide I (Z) 1685; Amide I (peptide) 1660. Amide II 1560, 1530;  $v_{as}$ C—C—O 1255;  $\gamma$ CC 700;  $\gamma$ (=CH) 745 cm<sup>-1</sup>.

#### 5 - (2,4-0-Benzylidene-1,2,3,4-tetrahydroxybutyl)-hydantoin-3-acetic acid (IV)

N-Carbobenzoxy-4,6-O-benzylidene-D-glucosaminoylglycine methyl ester (6.3 g; 0.013 mole) (III) was suspended in acetone (95 ml) with stirring at room temperature and 1 N sodium hydroxide solution (50.5 ml; 0.0504 mole) was poured to the suspension. The solid substance dissolved in a few minutes, and the solution was agitated for 1 hr, then the acetone was evaporated in vacuum (20  $^{\circ}$ C/15 torr) and the aqueous solution was acidified to pH 3 with 1 N hydrochloric acid at 0 °C. The aqueous solution was then extracted with ethyl acetate ( $40 \times 30$ ml; a total of 1200 ml) and the combined organic phase was washed with distilled water  $(3 \times 50 \text{ ml})$  until free from chloride ion, dried over anhydrous sodium sulfate; finally the solvent was evaporated in vacuum at room temperature. The crude product (3.15 g; 65%) was crystallized from ethanol (50 ml) to obtain 1.25 g of a white crystalline substance, m.p. 178-181 °C;  $R_f^3 = 0.34.$ 

C16H18N2O8 (366.337). Calcd C 52.46; H 4.95; N 7.65. Found C 52.45; H 4.83; N 7.85%. IR: νOH (carboxylic acid) 2400-3600; Amide I 1755, 1670; βNH 1400 cm<sup>-1</sup>.

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# β-ELIMINATION IN THE EINEORN ACETYLATION OF 4,6-0-BENZYLIDENE-2-BENZYLOXYCARBONYLAMINO--2-DEOXY-D-GLUCONIC ACID

# PRELIMINARY COMMUNICATION

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Recently, WHISTLER and HOFFMANN [1] described the decomposition of 1,2,3,5-tetra-O-acetyl-4-thio-D-ribofuranose to yield 2-acetoxymethyl-4-acetoxythiophene. Similar results were obtained by KUSZMANN and SOHÁR [2] who observed that 1,3,5-tri-O-acetyl-2-chlorodeoxy-D-arabinose partly decomposes into 2-acetoxymethyl-4-chlorofuran during vacuum distillation. The common feature of both reactions is the splitting off of acetic acid and the formation of a new carbon-carbon double bond. Recently we have observed a similar elimination reaction while trying to acetylate 4,6-O-benzylidene-2-benzyloxycarbonylamino-2-deoxy-D-gluconic acid 1 in pyridine with acetic anhydride. Contrary to the ethyl ester of the before mentioned D-gluconic acid 1 which can be transformed smoothly into its di-O-acetyl derivative, acetylation of 1 vielded a new compound 2 differing in composition and spectral data from the expected one. On the basis of IR (Table I) and analytical data, 2 is considered to be 2-benzyloxycarbonylamino-4,6-O-benzylidene-2,3-dideoxy-D-erythro-hex--2-enono-1,5-lactone (m.p. 190 °C). Formerly similar result has been reported for the corresponding N-benzoyl derivative [3]. This structure was confirmed by the NMR spectrum (Table I) which contained a doublet at  $\delta = 7.07$ characteristic of the olefinic (H-8) proton.



# Table I

The spectral data\* of compound 2

	Fr	equencies (cm <sup>-1</sup> )		Assignation			
	in KBr	in CHCl <sub>3</sub>					
	3410 3350	3400	$     \begin{array}{c}             \nu  \mathrm{NH} \\             pect \\             \nu  \mathrm{NH}         \end{array}     $	(monomeric and solvated, res- ively) (associated)			
	1740 1730	1725	v C =	O (lactone)			
1	1710	1710	ν C =	O (urethan)			
IR spectrum	1645 1635	1645	ν C =	C			
	1335 1325 1313 1215 1080 1020		v C-C	) (lactone and acetal)			
d stary d d stary d l stary d	753 748		γ C <sub>Ar</sub> I	I (monosubstituted benzene)			
udit nates d Intac≿ine t	698		$\gamma C_{Ar} C$	$\mathcal{L}_{Ar}$ (monosubstituted benzene)			
ant name La capa	Signal δ (ppm) or ν (Hz)	Multiplicity	Intensity	Assignation			
NMR spectrum	235-285 Hz 4.88 ppm 5.18 ppm 5.80 ppm 7.07 ppm 430-460 Hz 8.9 ppm	multiplet 2×doublet* singulet doublet** multiplet broad singulet	3H 1H 2H 1H 1H 1OH 1H	H-4, H-4', H-10 H-9 H-methylene of benzyl group H-2 H-8 H of phenyl groups NH			

\*  $J_{9,10} = 9$  Hz,  $J_{8,9} = 1.5$  Hz, \*\*  $J_{8,9} = 1.5$  Hz

\* The IR spectra were recorded in KBr pellets and in dilute  $CHCl_3$  solution with a Per-KIN-ELMER 457 instrument. The NMR spectrum (in hexadeuterodimethyl-sulphoxide) was obtained by using a Varian A-60D spectrometer, with tetramethylsilane as internal standard.

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### **RECTIFICATION OF MULTICOMPONENT MIXTURES, II**

### LOCAL AND GENERAL CHARACTERISTICS OF THE TRAJECTORIES OF RECTIFICATION PROCESSES AT INFINITE REFLUX RATIO

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The fundamental characteristics of the rectification trajectories in an ideal countercurrent apparatus at infinite reflux ratio are studied. It is demonstrated that in this case the continuous rectification ranges are characterized by the trajectory beam of the process located in a particular manner in the composition simplex. The steady-state points of the rectification process are junction and saddle type points. The boundaries between the rectification ranges pass through these points and their position depends on the distribution of resistance to mass transfer between the phases. The location of the trajectory beam in the composition simplex is determined by the structure of the liquid-vapour equilibrium phase diagram. A classification of the rectification ranges is given. The position of constant composition zones in the ideal countercurrent apparatus is investigated.

In a previous paper [1] the fundamentals of the thermodynamic-topological analysis of liquid-vapour equilibrium diagrams were established. By means of this analysis, the possible compositions of the final products of rectification, the sequence of the fractions and the principles of the separation technology can be qualitatively determined. We also demonstrated that in the general case, the composition simplex for an *n*-constituent mixture is composed of individual cells which were named ranges of continuous rectification [2]. Each rectification range in the composition diagram of a phase is characterized by a definite configuration. In the general case, the boundaries and the configuration of the rectification ranges depend on the character of the course of the process, the latter — in turn — being determined by the set of static parameters and by the type of the mass exchange apparatus. The static parameters include the reflux ratio R and the overall efficiency of the apparatus, *i.e.*, the number *n* of separation steps or the length *l* of the rectification co'umn, yielding the possible combinations shown in Table I.

	R	n(l)
I	infinite	infinite
II	infinite	finite
III	finite	infinite
IV	finite	finite

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	<b>CL 1</b>	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	0	

Combinations I and III correspond to the theoretically possible maximum separation of the mixture. These combinations cannot be realized in practice. However, as will be shown in the following, combination I can be successfully utilized in the analysis of rectification trajectory beams as a whole. Combination III is usually applied in column design for calculating minimum reflux ratios. Combinations II and IV are used in practice.

For the sake of simplicity, the course of rectification trajectories will be studied in the following on the example of mass exchange apparatuses with ideal displacement for both liquid and vapour phases. We also assume that the mass transfer coefficients  $\beta_i^{(x)}$  and  $\beta_i^{(y)}$  for the liquid and vapour phases, respectively, are identical for all constituents of the mixture being separated.

For an arbitrarily selected constituent *i*, the mass (in mols)  $dq_i$  passing from one phase to the other across unit area of the interface will be proportional to the mass transfer coefficient  $\beta_i$  and to the difference between the concentrations on the interface and in the interior of the stream:

$$egin{array}{lll} dq_i^{(\mathrm{x})} &= eta_i^{(\mathrm{x})}(x_i - x_i^{\mathrm{g}}) & ext{for the liquid phase} \ dq_i^{(\mathrm{y})} &= eta_i^{(\mathrm{y})}(y_i^{\mathrm{g}} - y_i) & ext{for the vapour phase} \end{array} egin{array}{llll} (1) & & \ext{for the vapour phase} \end{array}$$

where  $y_i$  and  $x_i$  are the concentrations of constituent *i* in the interiors of the vapour and liquid stream, respectively,

 $y_i^g$  and  $x_i^g$  are the concentrations of constituent *i* at the interface on the vapour and on the liquid side, respectively.

Let us assume that the concentrations at the interface are equilibrium concentrations, *i.e.*,  $y^g = K_i^g x_i^g$ , where  $K_i^g$  is the equilibrium distribution coefficient of constituent *i* between the liquid and vapour phases at their interface. Since  $dq_i^{(x)} = dq_i^{(y)}$ , the system of equations (1) yields

 $\beta_i^{(y)} y_i + \beta_i^{(x)} x_i = \beta_i^{(x)} x_i^g + \beta_i^{(y)} y_i^g \tag{2}$ 

Analogous equations can be established for each constituent of the mixture.

It follows from Eq. (2) that under the given assumptions for a mixture containing n constituents in an (n-1)-fold concentration simplex, the liquid-vapour node uniting the equilibrium compositions  $y_i^g$  and  $x_i^g$  at the interface has a point of intersection with the segment uniting the working concentrations  $y_i$  and  $x_i$ .

The coordinates of the point of intersection can be determined from the equation

$$x_{i}^{0} = \frac{\beta_{i}^{(y)}y_{i} + \beta_{i}^{(x)}x_{i}}{\beta_{i}^{(y)} + \beta_{i}^{(x)}} = \frac{\beta_{i}^{(y)}y_{i}^{g} + \beta_{i}^{(x)}x_{i}^{g}}{\beta_{i}^{(y)} + \beta_{i}^{(x)}}.$$
(3)

The point of intersection  $x_i^0$  divides the liquid-vapour node and the segment uniting the working concentrations into parts that are inversely proportional to the share of each phase in the resistance to mass transfer.

By dividing Eqs (1) by  $\beta_i^{(x)}$  and  $\beta_i^{(y)}$ , respectively, and adding the results, and also taking into account Eq. (2) and the equation  $y_i^g = K_i^g x_i^g$ , the following expression is obtained:

$$dq_{i} = \frac{\beta_{i}^{(x)}\beta_{i}^{(y)}}{\beta_{i}^{(y)}K_{i}^{g} + \beta_{i}^{(x)}} \left(K_{i}^{g}x_{i} - y_{i}\right).$$
(4)

By referring  $dq_i$  to 1 mol of the vapour phase and taking into account that

$$dq_i = \frac{dy_i}{dl} = \frac{mdx_i}{dl} \tag{5}$$

where m is tangens of the slope of the working line, Eq. (4) can be written in the form

$$\frac{dy_i}{dl} = \frac{\beta_i^{(x)}\beta_i^{(y)}}{\beta_i^{(y)}K_i^g + \beta_i^{(x)}} \left(K_i^g x_i - y_i\right)$$
(6)

for the vapour phase and

$$\frac{dx_i}{dl} = \frac{1}{m} \frac{\beta_i^{(x)} \beta_i^{(y)}}{\beta_i^{(y)} K_i^g + \beta_i^{(x)}} \left( K_i^g x_i - y_i \right) \tag{7}$$

for the liquid phase. The factor

$$\frac{\beta_i^{(x)}\beta_i^{(y)}}{\beta_i^{(y)}K_i^g + \beta_i^{(x)}}$$

will be designated by the symbol  $B_i$ .

Then, for an *n*-constituent mixture, the trajectory of the continuous rectification process which characterizes the composition change in the liquid phase along the height l of the column will be described by a system of autonomous differential equations:

$$\frac{dx_1}{dl} = \frac{B_1}{m} (K_1^g x_1 - y_1)$$

$$\frac{dx_2}{dl} = \frac{B_2}{m} (K_2^g x_2 - y_2)$$

$$\dots$$

$$\frac{dx_{n-1}}{dl} = \frac{B_{n-1}}{m} (K_{n-1}^g x_{n-1} - y_{n-1}).$$

An analogous system of equations is obtained for the vapour phase:

$$\frac{dy_1}{dl} = B_1(K_1^g x_1 - y_1)$$

$$\frac{dy_2}{dl} = B_2(K_2^g x_2 - y_2)$$

$$\dots$$

$$\frac{dy_{n-1}}{dl} = B_{n-1}(K_{n-1}^g x_{n-1} - y_{n-1}).$$

Since the distribution coefficients  $K_i^g$  are different for each constituent, we have  $B_i \neq B_j$ .

For the case of infinite reflux ratio,  $y_i = x_i$  and m = 1, consequently, the trajectories described by systems of equations (8) and (9) coalesce into a single trajectory corresponding to the following system of equations:

$$\frac{dx_1}{dl} = B_1 x_1 (K_1^g - 1)$$

$$\frac{dx_2}{dl} = B_2 x_2 (K_2^g - 1)$$

$$\dots$$

$$\frac{dx_{n-1}}{dl} = B_{n-1} x_{n-1} (K_{n-1}^g - 1).$$
(10)

Let us assume that the resistance to mass transfer is concentrated in the vapour phase. In this case the point corresponding to composition  $x_i^0$  (see Eq. (3)) coincides with the points  $x_i^g$  and  $x_i$ .

In fact, at m = 1  $(R = \infty)$  it follows from Eq. (3) that

$$x_{i}^{0} = x_{i} = \frac{\frac{1}{\beta_{i}^{(x)}} y_{i}^{g} + \frac{1}{\beta_{i}^{(y)}} x_{i}^{g}}{\frac{1}{\beta_{i}^{(x)}} + \frac{1}{\beta_{i}^{(y)}}} .$$
(11)

(9

If  $\frac{1}{\beta_l^{(x)}} = 0$ , it is evident that  $x_i^0 = x_i = x_i^g$  and, consequently,  $y_i^g = y_i^*$ , where  $y_i^*$  is the concentration of constituent *i* in the vapour in equilibrium with concentration  $x_i$  in the interior of the liquid stream.

Obviously  $y_i^* = K_i^* x_i$ , where  $K_i^*$  is the equilibrium distribution coefficient, and Eqs (10) will take the form

$$egin{aligned} rac{dx_1}{dl} &= eta_1^{(y)} x_1(K_1^*-1) \ rac{dx_2}{dl} &= eta_2^{(y)} x_2(K_2^*-1) \ rac{dx_{n-1}}{dl} &= eta_{n-1}^{(y)} x_{n-1}(K_{n-1}^*-1). \end{aligned}$$

Since it has been assumed that  $\beta_i^{(y)} = \beta_j^{(y)}$ , the coefficients  $\beta_i^{(y)}$  in this case play the part of scale coefficients. This can be proved by dividing all equations of system (12) by the equation for the (n - 1)th constituent:

$$egin{aligned} rac{dx_1}{dx_{n-1}} &= rac{x_1(K_1^*-1)}{x_{n-1}(K_{n-}^*-1)} \ rac{dx_2}{dx_{n-1}} &= rac{x_2(K_2^*-1)}{x_{n-1}(K_{n-1}^*-1)} \ rac{dx_{n-2}}{dx_{n-2}} &= rac{x_{n-2}(K_{n-2}^*-1)}{x_{n-1}(K_{n-1}^*-1)} \ . \end{aligned}$$

Equation system (13) is identical with the system of equations describing in differential form the trajectories of free equilibrium evaporation, *i.e.*, corresponding to the composition change of the liquid phase at free equilibrium evaporation.

In this case, each trajectory of the rectification process will fully coincide with the trajectory of the equilibrium distillation process, and the liquid-vapour nodes will be tangential in each point of the investigated trajectories.

Let us now assume that the resistance to mass transfer is concentrated in the liquid phase. In this case, taking into account that  $y_i = x_i$  and  $x_i^0 = y_i = y_i^g$ , equation system (10) will take the form

(12)

(13)

(14)

(15)

$$\begin{aligned} \frac{dy_1}{dl} &= \beta_1^{(x)} y_1 \left( 1 - \frac{1}{K_1^*} \right) \\ \frac{dy_2}{dl} &= \beta_2^{(x)} y_2 \left( 1 - \frac{1}{K_2^*} \right) \\ \dots \\ \frac{dy_{n-1}}{dl} &= \beta_{n-1}^{(x)} y_{n-1} \left( 1 - \frac{1}{K_{n-1}^*} \right) \end{aligned}$$

where  $K_i^* = \frac{y_i}{x_i^*}$ .

Since  $\beta_i^{(x)} = \beta_j^{(x)}$ , equation system (14) is equivalent to the following system of equations:

$$\frac{dy_1}{dy_{n-1}} = \frac{y_1 \left(1 - \frac{1}{K_1^*}\right)}{y_{n-1} \left(1 - \frac{1}{K_{n-1}^*}\right)}$$
$$\frac{dy_2}{dy_{n-1}} = \frac{y_2 \left(1 - \frac{1}{K_2^*}\right)}{y_{n-1} \left(1 - \frac{1}{K_{n-1}^*}\right)}$$
$$\dots$$
$$\frac{dy_{n-2}}{dy_{n-1}} = \frac{y_{n-2} \left(1 - \frac{1}{K_{n-2}^*}\right)}{y_{n-1} \left(1 - \frac{1}{K_{n-1}^*}\right)}$$

describing the process of free equilibrium condensation. In this case, each trajectory of the rectification process fully coincides with the trajectory of free equilibrium condensation, and the vapour-liquid nodes are tangential to these trajectories. In the general case, when the trajectories of free equilibrium evaporation and of free equilibrium condensation are not straight lines, they do not coincide. Consequently, the distribution of the constituents along the height of the column separating a mixture with identical distribution coefficients, but concentrating the resistance to mass transfer in different

### SERAFIMOV et al.: RECTIFICATION OF MULTICOMPONENT MIXTURES, II

phases, will differ. In view of the accepted assumptions, the trajectories of free equilibrium evaporation and of free equilibrium condensation are limiting trajectories. All other trajectories, corresponding to different cases of the distribution of resistance to mass transfer between the phases, are located between these limiting trajectories, and the liquid-vapour node (or vapour-liquid node) is tangential to the trajectories of the process in point  $x_i^0$  which divides the nodes into segments inversely proportional to the share of resistance to mass transfer in each phase.



Fig. 1. Liquid-vapour nodes tangential to the process trajectories at  $R = \infty$ . a – Resistance to mass transfer concentrated in the vapour phase; b – Resistance to mass transfer distributed between the phases; c – Resistance to mass transfer concentrated in the liquid phase

Some selected cases are presented in Fig. 1. The figure indicates that in all three cases the direction of the trajectories is determined by the direction of the liquid-vapour (or vapour-liquid) node in the diagram of the investigated multiconstituent mixture. The characteristic configuration of the node field in the concentration simplex can be used for the classification of the diagrams. Fig. 2 presents the liquid-vapour node fields for thermodynamically possible phase equilibrium diagrams in the case of a ternary mixture. This figure shows that each type of diagram is characterized by a particular node field, and consequently by a particular course of the trajectories of continuous rectification.

Let us investigate in general the local characteristics of the course of rectification process trajectories in the vicinity of steady-state points, *i.e.*, points in which the right sides of Eqs (10) simultaneously become zero. Since  $\beta_i$  is never equal to zero, two cases correspond to the condition of the zero solution, namely:

$$x_i = 0$$
 or  $K_i^g = 1$ 

which can appear in various combinations.

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Fig. 2. Liquid-vapour node field for diagrams of different classes and types. Steady-state points are marked by points. The first two digits represent the class of the mixture. The digit (and letter) after the dash represent the type and subtype of the mixture. Antipodes are obtained by reversing the direction of the nodes [1]

Let us assume that all distribution coefficients  $K_i^g$  are equal to 1. In this case the investigated steady-state point corresponds to the *n*-constituent azeotropic mixture located on the hyperboundary of the concentration simplex.

In the case when for (n - k) constituents  $K_i^g = 1$ , and for k constituents  $x_i = 0$ , the steady-state point corresponds to the azeotropic mixture consisting of (n - k) constituents.

If  $K_i^g = 1$  for one constituent and  $x_i = 0$  for (n - 1) constituents, the steady-state point corresponds to the pure constituent and is located at the vertex of the concentration simplex. Thus, only points corresponding to azeo-tropic mixtures or to pure constituents can appear as steady-state points of the trajectories of rectification at  $R = \infty$ .

It should be mentioned that in the case when  $K_i^g = 1$ , we have  $x_i = y_i$ and, consequently, if  $x_i = 0$ , then  $x_i^g = 0$ .

Let us investigate the course of the trajectories of the rectification process in the vicinity of the steady-state points. For this purpose, we shall shift the origin of the coordinate system to the steady-state point by introducing new variables  $\eta_i = x_i - x_i^{(z)}$  for each constituent, where  $x_i^z$  stands for the coordinate of the singular point in the concentration simplex.

The right sides of Eqs (8) are now expanded into Taylor series in terms of variable  $x_i$ , retaining only the linear terms. Taking into account that m = 1, a first approximation is obtained:

From the determinant of Eqs (16), the characteristic equation is

$$\begin{pmatrix} n^{n-1}\\ \mathbf{I}\\ \mathbf{I}\\$$

Since  $\prod_{i=1}^{n-1} B_i \neq 0$ , characteristic equation (17) is equivalent to the char-

acteristic equation studied in detail [3, 4] for the case of free equilibrium evaporation. According to the theorem of characteristic roots proved in Ref. [5], the roots  $\lambda_i$  of Eq. (17) will all be real. This means that the steady-state points on the trajectories of the rectification process at infinite reflux ratio will be either of the 'junction' or of the 'saddle' type. Consequently, the character of the trajectories in the vicinity of steady-state points is similar for equilibrium distillation, for equilibrium condensation and for continuous rectification at  $R = \infty$ . In the steady-state points of the 'junction' type all trajectories of the rectification process either enter this point or start from it.

In the case of steady-state points of the 'saddle' type, part of the trajectories enters them or starts from them, while the others proceed hyperbolically in the vicinity of this point. Taking into account the similar course of trajectories in the vicinity of steady-state points for the different processes listed above, the results reported in [4-9] can be utilized for elucidating various local characteristics of the rectification process.

A 'range of continuous rectification' at infinite reflux ratio refers to the multitude of compositions in the concentration simplex in which all trajectories of the rectification process have one initial steady-state point of the 'unstable junction' type and one steady-state end point of the 'stable junction' type. Thus, each rectification range has a corresponding characteristic trajectory beam with two 'junction-type' steady-state points. These ranges, composed of ordinary trajectories, are separated from each other by separatrices of saddle-type steady-state points. These latter are particular trajectories of the rectification process, proceeding from the junctions to the saddles or in the reverse direction. For ternary mixtures, the saddle separatrices are lines, for four-constituent mixtures they are surfaces, for fiveconstituent mixtures volumes, etc. A trajectory or a set of trajectories of this type is regarded as a separate range of continuous rectification, characterized by definite steady-state initial and end points. These points of trajectory beams belonging to one rectification range are in the investigated case minimum and maximum boiling temperatures within the temperature field characterizing the range in question. Along each trajectory (no matter whether ordinary or particular) the derivative of the temperature retains its sign along the height of the column. We shall show this on the example of ternary mixture, utilizing the van der Waals equation connecting the distribution coefficients  $K_{i}^{g}$  of the constituents with the temperature and pressure of the coexisting phases [10].

For ternary mixtures at constant pressure this equation takes the following form:

$$egin{aligned} &\eta_{(x,y)}\,dT = \left[\zeta_{il}x_{l}^{g}(K_{l}^{g}-1)+\zeta_{ij}x_{j}^{g}(K_{j}^{g}-1)
ight]dx_{l}^{g}+ \ &+\left[\zeta_{ji}x_{l}^{g}(K_{l}^{g}-1)+\zeta_{jj}x_{j}^{g}(K_{j}^{g}-1)
ight]dx_{j}^{g} \end{aligned}$$

where  $\eta_{(xy)}$  – entropy of phase transition,

- $\zeta_{ij}$  second derivative of the Gibbs potential with respect to concentration,
- T temperature.

Taking into account that  $x_i = y_i$ , Eq. (2), after rearrangement, yields

$$\beta_i \boldsymbol{x}_i^g = \boldsymbol{B}_i \boldsymbol{x}_i \tag{19}$$

where  $rac{1}{eta_i}=rac{1}{eta_i^{(\mathbf{x})}}+rac{1}{eta_i^{(\mathbf{y})}},$ 

By solving Eq. s (10) and (19) jointly, the following system of equations is obtained:

By substituting the expression for  $\frac{dx_i}{dx_j}$  obtained from the equation system (20) into Eq. (18) and some rearrangement, the following equation is obtained  $\frac{dT}{dl} = -\beta_i \frac{(K_i^g - 1)^2 (x_i^g)^2 \zeta_{ii} + 2(K_i^g - 1) (K_j^g - 1) x_i^g x_j^g \zeta_{ij} + (K_j^g - 1)^2 (x_j^g)^2 \zeta_{jj}}{\eta_{xy}}$ . (21)

Since the numerator and denominator in the right side of Eq. (21), as well as  $\beta_i$ , are always positive, the derivative  $\frac{dT}{dl}$  does not change its sign when moving from one steady-state point to another within the boundaries of one trajectory beam.

Under conditions when the steady-state point has been reached by several constituents,  $K_i = K_j = 1$ , while for the rest of the constituents  $x_i^g = 0$  and consequently  $\frac{dT}{dl} = 0$ . In this case  $l \to \infty$ , *i.e.*, a constant temperature zone will be observed in the rectification column corresponding to a constant composition of the mixture being separated. Thus, whatever the distribution of the resistance to mass transfer between the phases, each trajectory of the rectification process has one and only one point of intersection

(20)



Fig. 3. Isotherm-isobar topographic systems for the diagrams corresponding to different classes and types. The first two digits represent the class, the following digit and letter refer to the type and subtype

with the isotherm-isobar. Consequently, the topographic system of isothermsisobars unequivocally characterizes the qualitative course of the trajectories

at infinite reflux ratios. By way of example, Fig. 3 presents the thermodynamically possible topographic systems of isotherms-isobars for ternary mixtures [3].

The correspondence between the trajectory system of the rectification process and the topographic system of temperatures is manifested by 'junction' type steady-state points in the trajectory diagram appearing as 'centre' type steady-state points in the topographic system, and saddle-type steady-state points corresponding to saddles.

Our analysis has shown that the course of the trajectories of continuous rectification differs at different shares of the contacting phases in the resistance to mass transfer. It follows from this that in the general case, the boundaries of the rectification ranges (defined as the multitude of trajectories proceeding from the junction to the saddle or reversely) are mobile and depend on the distribution of the resistance to mass transfer between the phases. Only the steady-state points corresponding to azeotropic mixtures and to pure constituents are immobile in the trajectory diagram. The limiting location of the boundaries is determined by trajectories forming a multiplicity which separates the composition simplex into distillation ranges and a multiplicity separating the composition simplex into condensation ranges. In the specific case of ternary mixtures, each of these multiplicities consists of one trajectory or of a finite number of trajectories.

It is known [11, 12] that the class, type and subtype of the diagram is determined by the total number and relative position of singular points of the 'junction' and 'saddle' type. As shown in the foregoing, a characteristic 'pattern' of trajectory beams in the concentration simplex corresponds to each kind of diagram. In ternary systems, all rectification ranges can be subdivided into five groups, depending on the pattern of trajectory beams. It should be noted that the trajectory beam patterns are independent of the distribution of the resistance to mass transfer between the phases both within the limits of one range and in the diagram as a whole.

The first group includes ranges whose configuration, in the general case, is a curvilinear triangle. The ranges belonging to this group are characterized by the presence of two 'junction' type points  $N_0$  and of one 'saddle' type point  $C_0$  representing a hyperbolic segment of the 'saddle'. In particular, this is the principle of the trajectory diagram at  $R = \infty$  for zero class mixtures [1]. This kind of diagram is presented in Fig. 4a.

The second group consists of rectification ranges with a deformed quadrangular configuration. These ranges are characterized by the presence of two junction points  $N_0$  and two saddle points  $C_0$ . This group is further divided into two subgroups. In the first subgroup, the points  $N_0$  and  $C_0$  alternate (Fig. 4b), in the second subgroup the points  $N_0$  and  $C_0$  are arranged in pairs (Fig. 4c).



Fig. 4. Examples for different groups of rectification ranges

The third group consists of rectification ranges containing three saddle points  $C_0$  at the boundary and two junction points  $N_0$ . Geometrically, this group corresponds to a deformed pentagon where two  $C_0$  points are located next to each other on the boundary line and the third  $C_0$  point between two  $N_0$  points (Fig. 4d).

The fourth group consists of rectification ranges containing two  $N_0$  points and four  $C_0$  points. These ranges correspond to a deformed hexagon

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in which two adjacent sides are bonded to each other. Cases are possible where pairs of  $C_0$  points are separated by  $N_0$  points (first subgroup) (Fig. 4e). In the ranges forming the second subgroup, three  $C_0$  points are adjacent and one  $C_0$  point is located between two  $N_0$  points (Fig. 4f).

The fifth group of rectification ranges corresponds to the case where two  $N_0$  points and five  $C_0$  points are present. The configuration is that of a heptagon with two adjacent sides bonded (Fig. 4g).

Depending on the type of the rectification range, local extrema for the individual constituents are observed along the trajectories. In ideal countercurrent columns, a local extremum in the concentration of the constituent *i* corresponds to the condition  $y_i^g = x_i^g$ , *i.e.*,  $K_i^g = 1$  for this constituent. A number of multitudes located characteristically in the concentration simplex



Fig. 5. Thermodynamically possible diagrams of the  $K_i = 1$  lines. The first two digits represent the class, the digit after the dash refers to the type, the Latin letter represents the subtype and the Greek letters denote diagrams with particular deformation of the rectification trajectories at infinite reflux ratio

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In thermodynamically possible liquid-vapour equilibrium diagrams for threeconstituent mixtures satisfy the condition that the distribution coefficient of an individual constituent be equal to 1. By way of example, Fig. 5 presents the lines  $K_i = 1$ . By comparing Fig. 5 and Fig. 3, it can be seen that in individual cases several diagrams of the  $K_i = 1$  lines may correspond to one and the same diagram with a characteristic pattern of isotherms-isobars. This type of diagrams, analogously to the diagrams of the trajectories of free equilibrium evaporation [12] might be called diagrams with discriminated deformation of the trajectories of rectification and — retaining the class, type and subtype of the diagrams — might be denoted by the symbols  $\alpha$ ,  $\beta$ ,  $\gamma$ .

Figs 3 and 5 also indicate that a line  $K_i = 1$  passes through the vertex *i* of the triangle through which an isotherm-isobar of finite dimension passes. In this case this vertex appears in the trajectory diagram [12] as a segment of the saddle  $C_0$ , *i.e.*, as a steady-state point of the saddle type. Two lines  $(K_j^g = 1 \text{ and } K_j^g = 1)$  pass through both junction and saddle type steady-state points located on the sides of the Gibbs triangle *ij*. These points correspond to binary azeotropic mixtures. Three lines fulfilling the condition  $K_i^g = 1$ ,  $K_j^g = 1$  and  $K_k^g = 1$  pass through the steady-state points of the junction and saddle type, respectively, corresponding to ternary azeotropic mixtures.

For any rectification trajectory located in the interior of the rectification range, the constant temperature zones at  $l \rightarrow \infty$  corresponding to zones of constant concentration  $x_i = \text{const.}$  are located at the initial and final points of the trajectory. (The zones of constant concentration are usually called constant concentration ranges, CCR.) These points are steady-state points of the liquid-vapour equilibrium diagram and correspond — as shown before to azeotropic mixtures and to pure constituents. Thus, the number of such zones is two for any ordinary rectification trajectory. The characteristic S-shape of the temperature curve along the height of the column is shown in Fig. 6a for the case of ordinary trajectories located in the interior of the rectification range.

The sequence of simple non-steady state points on any trajectory corresponds to finite-length, ideal displacement rectification columns.

Therefore, if it is assumed that the process is interrupted at a definite concentration in one or two cross-sections of the apparatus, the length l of the column working within the chosen concentration range will correspond either to a finite or to an infinite, but definitely to only a single CCR zone. Thus, three cases can be distinguished at  $R = \infty$ :

1.  $l = \infty$ , two marginal CCR zones exist,

2.  $l = \infty$ , one marginal CCR zone exists,

3. l = finite, no CCR zones exist.

The last case corresponds to the minimum length of the column capable of performing the required separation (set of conditions II in Table I). Thus,

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Fig. 6. Temperature gradient along the height of the column at different number of constant composition zones along the boundary trajectories of the rectification process. a - 2 CCR zones, b - 3 CCR zones, c - 4 CCR zones, d - 5 CCR zones, e - 6 CCR zones, f - 7 CCR zones

the trajectories of the set of conditions II represent part of the trajectories of the set of conditions I, and consequently are fully enclosed within the limits of the continuous rectification range characteristic for the given distribution of resistance to mass transfer between the phases.

The trajectories coinciding with the boundaries of the rectification range are of particular interest. The highest and lowest boiling temperatures of the mixtures whose concentrations correspond to the boundaries of the rectification ranges are steady-state points of the junction type, while the temperature corresponding to steady-state points of the saddle type is an intermediate temperature within the given temperature range. Therefore, the rectification trajectory may extend from one junction point to the other, while passing through one or several points of the saddle type. In the ranges corresponding to saddle-type steady-state points, CCR zones will be observed which — in contrast to the boundary zones corresponding to junction-type steady-state points — will be located in the middle of the rectification column. It is worth mentioning that in this case, ternary saddle-type azeotropic mixtures may also appear as non-terminal points of the trajectory. These will then correspond to a CCR zone located in the middle of the column.

In fact, the rectification apparatus appears in the investigated cases as if it were composed of individual columns, each separating qualitatively

differing mixtures. Actually, the transition from one part of the column through a CCR zone to another part is accompanied by the disappearance of a constituent, while another constituent may appear in the subsequent part of the column.

Since the number of CCR zones along the boundary trajectories is equal to the number of steady-state points and the initial and final steady-state points are always junction-type points, in the general case the number Sof the CCR zones for the boundary trajectories is equal to the number of saddle-type steady-state points  $C_0$  located one after the other on this trajectory, +2:

$$S = C_0 + 2 \tag{22}$$

In Fig. 6, the different cases of CCR zone location along the parts of the column are presented. It can be seen from the figure that the maximum number of CCR zones for the boundary trajectories corresponding to the set of conditions I is 7 and the minimum number is 2. The demonstrated characteristics of the behaviour of trajectories on the boundary of rectification ranges are very interesting, because in this case fractions of pure constituents having medium volatility and fractions of azeotropic mixtures will be present as intermediate fractions. This appears to be a generalization of the known theorem of limiting trajectories for ternary mixtures, according to which, the pure constituent having a medium volatility value as compared to the two other constituents can appear as a fraction corresponding to a CCR zone [13]. In this case, only one saddle-type steady-state point exists, lying on the boundary of the Gibbs triangle and corresponding to the pure constituent having medium volatility (*cf.* diagram of the zero class in Fig. 2, corresponding to azeotropic and partly to ideal mixtures).

In principle, the set of conditions II on the boundaries of continuous rectification ranges is also realizable. If the boundary passes through the interior of the Gibbs triangle, this case does not differ at all from the case of ordinary trajectories. If the trajectory of the process coincides with the side of the Gibbs triangle, this case corresponds to the separation of an ordinary binary mixture in a column of minimum length, capable of separating the mixture in question.

Thus, at  $R = \infty$ , the continuous rectification ranges are characterized by the trajectory beam corresponding to the set of conditions I. The compositions of the final products corresponding to the set of conditions II are located within the limits of the given ranges. The boundaries between the ranges are determined by the limiting trajectories of the beam, passing from junction to junction through saddle-type steady-state points. Each trajectory beam, corresponding to an individual rectification range, is characterized by its closedness. The character of the position of the beam within one range and

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the relative location of the beams in the Gibbs triangle do not depend on the distribution of the resistance to mass transfer between the phases, but are determined by the structure of the liquid-vapour equilibrium diagram, *i.e.*, by the location of liquid-vapour nodes and isotherms-isobars in the diagrams in question. In the case of ideal displacement apparatus, the position of the boundaries between the rectification ranges depends on the distribution of resistance to mass transfer between the phases.

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### RECENSIONES

### Kinetics and Mechanism of Polyreactions

IUPAC International Symposium on Macromolecular Chemistry. Plenary and main lectures

Edited by F. TÜDŐS. Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences), Budapest 1971. LII sheets, 808 pp., 457 figures, 149 tables

The volume contains 4 plenary and 35 main lectures presented at the IUPAC International Symposium on Macromolecular Chemistry held in Budapest from 25th to 30th August, 1969.

The subject of the volume: kinetics and mechanism of polyreactions and related problems in the synthesis and chemistry of plastics and high polymers. The volume gives a comprehensive view of general results attained in the field of polymers.

It deals mainly with the following subjects:

Polyaddition and polycondensation Cationic, anionic and radical polymerization Ionic coordination polymerization Radiation and photochemical polymerization Polymerization in heterogeneous systems Polymerization in the solid phase Grafting and cross-linking Polymer-analogous reactions Depolymerization, degradation and stabilization of polymers

The contributors of the volume are outstanding scientists and researchers of international repute. The scientific material of the book comprises the most important results of kinetic and mechanism research carried out in the field of high polymers and should be of considerable use for all scientists interested in the field of macromolecular chemistry in gaining a view of the recent achievements in this field.

Owing to its content, the volume will undoubtedly win high acclaim among macromolecular chemists for its close relation to subjects originating or rapidly developing during the last years.

The work is of great interest for specialists in the field of polymers enabling them to apply the most recent concepts to their own work.

The printing of the book is very good; the formulas and figures are clear, misprints and errors were not found.

In summary, it is the opinion of the reviewer that the book is written in a coherent way and is easy to handle. It may be recommended to specialists of high polymers, as well as advanced students specialized in macromolecular chemistry.

I. Géczy

### XXIIIrd International Congress of Pure and Applied Chemistry

Boston, USA, 1971. Special Lectures. Butterworths, London, 1971

IUPAC organized at the end of July 1971 its XXIIIrd congress, and the special lectures were available already four months later, in December 1971, in the form of a book of about 2500 pages, in 8 volumes, to the readers interested.

This world record of publishing was made possible by the photomechanical reproduction of the original manuscripts. This rapidity went naturally somewhat to the expense of quality, and in some places even the page numbering is problematic. But this shortcoming is by far surpassed by the advantage that the text of the papers can be studied already at a time when they have not yet lost their actuality. At such a huge congress, even participants cannot attend each lecture of interest to them. The possibility of quiet meditation over a written text means, therefore, an enormous advantage for everybody.

Volume 1, 417 pp. (US \$ 15), comprises the lectures of the following sections: a) "Application of quantum mechanics to organic reaction paths", 8 papers (M. J. S. DEWAR, F. FUKUI, etc.) on 175 pages. b) "Intermolecular rearrangements, valence isomerization and cycloaddition, 7 papers (e.g. R. HUISCEN, E. DOERING, etc.) 136 pages; c) "Photochemistry", ' papers (e.g. O. L. CHAPMAN, D. ELAD, etc.).

Volume 2, 337 pp. (US \$ 12), contains: a) "General methods of synthesis". In this part (5 papers, 120 pages), the lecture of E. J. COREY is of particular interest. It deals with the computerized design of the synthesis of complex organic molecules. b) "New natural product synthesis" (4 papers, 111 pages). From the printed text the paper of R. WOODWARD on vitamin  $B_{12}$  synthesis has been regrettably left out (obviously upon the request of the lecturer). The author has reported on the completion of this work in February 1972, at the IUPAC symposium in New Delhi on natural organic substances. c) "Small rings" (8 papers). In this part, we can read the text of the envisaged lecture of E. SCHMITZ, which could not be presented by the author in person.

Volume 3, 131 pp. (US \$ 7.50), with the following parts: a) "Medicinal Chemistry" (4 lectures, 54 pages), among these C. DJERASSI: "Reversible fertility control." b) "Insect chemistry" (3 papers) with an introduction from A. J. BIRCH.

Volume 4 (540 pp., US \$ 18). a) "Short-lived intermediates", the text of 10 lectures on 222 pages, including among the authors N. KORNBLUM, G. A. RUSSEL, and others. b) "Free radical and homolytic mechanisms" (153 pp.) 6 lectures, including those of P. D. BARTLETT, N. M. EMANUEL, etc. c) "Ion pair processes", 7 lectures (e.g., the papers of V. A. KABANOV, M. SCHWARZ, etc.).

Volume 5 (128 pp., US \$ 7.50), contains: a) "Biosynthesis", 110 pages with 4 lectures (A. R. BATTERSBY, E. VAN TAMELEN, etc.). b) The section "Mechanism of enzyme action" includes only the paper of F. H. WESTHEIMER.

Volume 6 (296 pp., US \$ 12), comprises the papers of the following sections: a) "Organotransition metal chemistry", 6 lectures on 168 pages, including among others the papers of R. MASON, A. W. JOHNSON. b) "Homogeneous catalysis" contains 4 papers (D. G. H. BALLARD, G. P. CHIUSOLI, etc.).

Volume 7 (279 pp., US \$ 12), reports on three sections: a) "Spectroscopy in structure determination" (9 lectures on 192 pages). The discussion of C-13 NMR spectroscopy by J. D. ROBERTS is of particular interest. In addition, we cite by way of example the lecture of R. C. LORD on laser-Raman spectroscopy, and that of E. HEILBRONNER on photoelectron spectroscopy. b) "Advances in conformational analysis" (53 pp.). After an introduction by D. BARTON, it contains the lectures of F. A. BOVEY, M. GOODMAN and E. L. ELIEL. c) "Synthesis and conformation of biopolymers." The section is represented by the text of three lectures (e.g., R. B. MERRIFIELD and B. GUTTE).

The arrangement of the volumes makes it possible for each reader to purchase the text of papers read in the sections corresponding to his sphere of interest.

Cs. SZÁNTAY

#### RECENSIONES

### XXIIIrd International Congress of Pure and Applied Chemistry. Vol. 8.

Special Lectures presented at Boston, USA, July 26-30, 1971. Butterworths, London, 1971. 317 pp.

Volume 8 contains 19 lectures from the field of macromolecular chemistry.

The first four papers deal with the photochemistry of macromolecular substances. Two lectures discuss the photochemistry and the excited states of proteins (F. W. J. TEALE) and nucleic acids (H. E. JOHNS), while two lectures treat the photochemical degradation of polymers (J. F. RABEK) and energy transfer and energy migration within the polymers (G. GEUSKENS, C. DAVID). The first two papers furnish new information on the structural analysis of biopolymers, while the latter two on the new possibilities of photostabilization and photochemical synthesis. The lecture of J. BOON gives valuable new data on the detailed mechanism of the stereoselective polymerization of olefins with Ziegler catalysts, while the paper of V. P. ZUBOV reports on new possibilities of the control of polymerization and copolymerization processes in the presence of complex-forming additives. The next six papers deal with the kinetic problems of chemical reactions occurring in polymers (N. A. PLATÉ and A. D. LITMANOVICH), with the relationship between their physical properties and chemical reactivity (H. MOREVETZ), with methods for the preparation of polymers with redox properties (H. G. CASSIDY) and finally, with the cross-linking by gamma-irradiation of aqueous polymer solutions (E. KIRAN, F. RODRIGUEZ). The topics of these papers permit to conclude that a study of the chemical transformations of polymers already formed opens up new possibilities for the acquiring of new knowledge. The lecture on the relationship between the morphology and the properties of block-polymers (R. T. LA FLAIR) is followed by a report on the advances in the synthesis of ethylene-propylene terpolymer elastomers (E. W. DUCK, W. COOPER). The next five lectures discuss the internal surface and adhesion problems of reinforced polymer systems, with particular regard to the interaction problems of glass, fibers and polymers. Modern materials of construction on polymer basis are almost without exception reinforced systems, and this circumstance underlines particularly both the theoretical and the practical importance of the five lectures completing the volume.

In summary, it can be seen from the review given above that the 19 lectures contained in Volume 8 give a certain picture on the lectures of macromolecular chemistry in Boston, but the reviewer thinks that the availability in good time of the manuscripts to the editor played a greater role in the selection of the lectures included in the volume, than the critical evaluation of all the lectures presented at the Congress. Many very important lectures were delivered at the Congress in Boston on recent results in macromolecular chemistry, which, regrettably, are not included in the volume. Gy. HARDY

### **R.** GOMPPER (editor): Cycloaddition Reactions

IUPAC Symposium, Munich 1970. Specially Invited Lectures. Butterworths, London, 1971. 108 pp.

The papers included in this book were also published in Pure and Applied Chemistry (Vol. 27, No. 4, 1971).

The paging of the book starts from 597 and its reason is not indicated. Of the material of the Symposium, the text of five lectures is included, together with detailed reference lists for each. This latter supplement provides a considerable advantage as compared with the simple reproduction of the oral presentation.

The first paper (P. D. BARTLETT, 13 pages) deals with some borderline cases of cycloaddition; within this very concisely and effectively discusses concerted (2 + 2) cycloadditions and the (2 + 2) addition of singlet oxygen.

In the lecture of H. BESTIAN (23 pages) the cycloaddition of sulfonyl isocyanates on isolated double bonds, allenes, ketenes, 1,3-dienes and acetylenes are treated. Similarly to BARTLETT, CH. S. FOOTE also discusses the mechanism of addition of

Similarly to BARTLETT, CH. S. FOOTE also discusses the mechanism of addition of singlet oxygen to olefins and other substrates very interestingly on 12 pages.

G. M. J. SCHMIDT deals with a relatively new and very difficult field, the photodimerization in the solid state (31 pages). The lecture is, unfortunately, a posthumous work, as the author died in 1971. This very precisely written and highly interesting paper acutely reminds the reader of the great loss caused by the death of this outstanding researcher of photochemistry.

The author of the last paper is N. J. TURRO, another outstanding worker in photochemistry (Cycloaddition reactions of carbonyl compounds possessing high energy content).

It is a pity that some other lectures that also aroused great interest (e.g., the paper by R. WOODWARD) is not published in the book which has been edited carefully, in good typographical presentation and with a short period of publication.

Cs. SZÁNTAY

### J. TÖLGYESSY, T. BRAUN, M. KYRS: Isotope dilution analysis

### Akadémiai Kiadó, Budapest, 1972. p. 194.

This recent book of the well-known authors, to which Professor HAÏSSINSKY wrote a commendatory preface, fills a gap, as it is the first monograph on isotope dilution methods, playing a role of steadily increasing importance in radioanalysis. Isotope dilution methods can be used conveniently in trace analysis, for the determination of substances of closely related structure, which, therefore, are difficult to separate, particularly in the fields of organic chemistry and biochemistry, for testing the purity of radioactive preparations, for solving problems in the determination of geological age, for the evaluation of various physico-chemical problems, etc.

The well systematized subject, written in a lucid-style, is divided into six main chapters. The first chapter deals with the theory of the isotope dilution methods, such as direct, reversed, derived and double isotope dilution, and with the application of the substoichiometric principle to direct and reversed isotope dilution. It discusses further the accuracy and sensitivity of the isotope dilution methods. The second chapter makes the reader acquainted with experimental techniques, procedures used for separation, and with the modes of determining the quantities of substances separated. The third chapter gives well selected determinations, important from the point of view of practice, from the field of inorganic chemistry, the fourth chapter from those of organic chemistry and biochemistry. The fifth chapter deals with the principles, practical realization and possible applications of isotope dilution performed with stable isotopes, while the sixth chapter with the application of isotope dilution to some special problems, such as measurement of volume, solubility, determination of the quantity of carriers, of dissociation constants, ion exchange capacity, etc. Ample literature at the end of each chapter helps the reader in further orientation. The authors discuss in addition to the advantages of the different isotope dilution methods also their limitations and the possible sources of error. A further merit of the authors is that they have succeeded in creating order in the jungle of isotope dilution methods, described in the literature by various names, though they are similar in principle or sometimes even identical.

This monograph, published by Akadémiai Kiadó, may greatly contribute to the use in a wider field of the isotope dilution method, an analytical tool of high sensitivity, which can be used efficiently for a wide variety of purposes. Indeed, as indicated also by the authors, owing to the relatively low level of radioactivity, the practical realization requires only an isotope laboratory, which can be built at not too high costs. The equipment of the laboratory costs only slightly more than that of the customary laboratories for instrumental analysis, while a whole series of radioactive preparations of the required purity and specific activity can be obtained on the market.

É. BÁNYAI

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### РЕЗЮМЕ

### Газовохроматографический анализ окисей азота, II

### Анализ NO<sub>2</sub> с помощью газовохроматографического реактора

Ц. Э. ДЁРИНГ, Р. ГЕЙЕР и П. РЁСКЕ

С помощью газовохроматографического реактора была изучена реакция NO<sub>2</sub> с различными фосфорорганическими соединениями, включая фосфины и фосфиты. Было найдено, что с трифенилфосфитом реакция протекает стехиометрически с образованием NO. Описываются соответствующие условия реакции, а также использование реакции для анализа смесей, содержащих различные составляющие части.

### Валентные колебания NH в области ниже, чем 3000 см<sup>-1</sup>, VIII

Циклические димерные структуры. Производные тиазолина и тиазина

### п. ШОХАР и Л. ТОЛЬДИ

С помощью ИК спектроскопии было доказано, что N-арил-тиомочевины реагируют с  $\alpha$ ,  $\omega$ -дигалоалканами, давая соединение со структурой II. ИК спектры этих соединений значительно отличаются от спектров соответствующих тиазолинов и тиазинов (I). Различия в спектрах соединений последних двух типов делают возможными две таутомерные структуры 1a и 1b. Ассоциационные структуры этих трех типов соединений в твердом состоянии также различаются.

### Структура карбетокси- и ацетил-производных 2-ариламинотиазолинов, -тиазинов и 1-арил-2-имино-тиазолинов

### п. шохар, л. тольди и к. фараго

Карбетоксилирование 2-имино-З-арил-тиазолидинов приводит к ацил-имино-производным, структура которых была доказана появлением низковолновой (1670 см<sup>-1</sup>) карбонильной полосы в ИК спектре. Это подтверждает также полагаемую структуру исходного материала.

исходного материала. Ацилирование 2-ариламино-тиазолинов теоретически может давать два изомера. По согласующимся данным ИК и ЯМР спектров карбетокси- и ацетил-производных, были образованы лишь 2-замещенные соединения. В случае аналогичных тиазинов изомеры могут быть различены лишь по ЯМР спектрам, т. к. карбонильная частота, находящаяся для тиазолинов около 1750 см<sup>-1</sup>, в спектрах тиазинов лежит между 1745 и 1705 см<sup>-1</sup>. Данные ЯМР показывают, что, за исключением одного случая, где образуются два изомера, ацильная группа всегда присоединяется к экзоциклическому азоту также и в тиазинах.

### Исследование металлических хелатов смешанных аминокислот

### М. В. ЧИДАМБАРАМ и П. К. БХАТТАХАРЯ

Было исследовано равновесие  $[MA]^- + L^- \rightleftharpoons [MAL]^{-2}$ , где M = Cu, Ni; A — нитрилотриуксусная кислота, L — глицин или аланин. Константы стабильности были определены с помощью техники Эрвинга — Розотти. Было найдено, что при низких pH образуются комплексы MA с составом 1 : 1, которые при повышенных pH стабильны. Константы стабильности комплекса со смешанным лигандом ( $K_{MAL}$ ), выраженные в логарифмах, приблизительно на две-четыре единицы меньше, чем для исходного комплекса металла с амином. Сравниваются и интерпретируются константы стабильности комплексов Ni(II) и Cu(II) смешанными лигандами.

### Электронографическое исследование строения молекулы N, N'-тио-бис-(диметиламина)

### И. ХАРГИТТАИ и М. ХАРГИТТАИ

Электронографическим методом было изучено строение молекулы N,N-тио-бис-(диметиламина) —  $(CH_3)_2$  NSN  $(CH_3)_2$  в газовой фазе. Методом наименьших квадратов были получены следующие длины связи и валентные углы: C—N 1.473  $\pm$  0.006 Å, S—N 1.688  $\pm$  0.006 Å, S—N—C 117.9  $\pm$  0.6°, C—N—C 116.5  $\pm$  1.6°, N—S—N 114.5  $\pm$  1.6°. Основная форма внутреннего вращения оказалась аналогичной со случаем (CH<sub>3</sub>)<sub>2</sub> NSON (CH<sub>3</sub>)<sub>2</sub> и (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>Cl в газовой фазе и (CH<sub>3</sub>)<sub>2</sub>NSO<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> в кристаллической фазе. Обсуждаются некоторые тенденции в изменениях конфигураций связей атомов серы и азота.

### БЕНЗАЗЕПИНЫ, V

### Дальнейшие исследования 2,3-дигидро-1H—[1, 5]-бензодиазепинов и 2,3-дигидро-[1, 5]-бензотиазепинов

### К. ХИДЕГ и О. ХИДЕГ-ХАНКОВСКИ

2,3-Дигидро-[1, 5]-бензодиазепины и -тиазепины могуть быть получены за счет конденсации о-фенилендиаминов или о-аминотиофенолов с различными β-замещенными кетонами. Дигидро-производные могут быть восстановлены до тетрагидро-соединений: оба типа соединений легко подвергаются ацилированию. Были приготовлены также дигидро-пиримидино- и дигидропиридино-диазепины.

### Изучение флавоноидов и модельных соединений с помощью ИК спектроскопии, IV

## Исследование вращательных изомеров 2'- и 2',6'-замещенных халконов

### 3. ДЫНЯ и ДЬ. ЛИТКЕИ

Свойства ИҢ спектров 2'- и 2', 6'-замещенных халконов были исследованы с помощью различной техники снятия спектров. Было установлено, что для изученных соединений в области валентных колебаний карбонила наблюдается двойное поглощение. На основе аналогий, взятых из литературы, это явление объяснялось присутствием S-цис и S-транс ротационных изомеров. Были исследованы структурные факторы, влияющие на появление ротационных изомеров, и на основе экспериментальных данных полагалась вероятная форма конформации этих соединений.

### Стероиды, ХХІ

## Сравнительные кинетические исследования реакции образования оксимов из стероидных кетонов

### И. ГААЛ, Б. МАТКОВИЧ, И М. МАРИК

Кинетические и термодинамические данные реакции образования оксимов из стероидных кетонов, изученной авторами, были сравнимы и рассмотрены с данными образования из других карбонильных соединений.

Согласно экспериментальным данным, реакция образования оксимов, с кинетической точки зрения, может быть хорошо описана уравнением скорости второго порядка.

На основе кинетических и термодинамических данных можно делать заключения относительно стереохимических, термодинамических и реакционноспособных свойств, играющих роль в образовании оксимов.

### Исследования в области ароматических сульфенилхлоридов, VI

### Реакция сульфенилхлорида с С-арилокси-N-арил-иминометан-Sоксидами

### Ф. КЛИВЕНИ, Г. ШТАЙЕР, А. Е. САБО и Й. ПИНТЕ

Была изучена реакция различных замещенных С-арилокси-N-арил-иминометан-Sоксидов, а также таутомеров сульфеновой кислоты этих соединений с п-толил-сульфенилхлоридом. Было установлено, что в реакции принимает участие один из таутомеров сульфеновой кислоты, образующийся при выделении соляной кислоты из сульфенилгалоида, давая при этом соответствующий эфир S-п-толил-тиолсульфиновой кислоты. Благодаря этим исследованиям были выяснены условия образования тиолсульфинатов из сульфенилхлоридов. Строение исходных веществ и продуктов реакции подтверждалось на основе ИК спектроскопических исследований.

### Ректификация многокомпонентных смесей, ІІ

## Локальные и общие закономерности траекторий процесса ректификации при бесконечном флегмовом числе

Л. А. СЕРАФИМОВ, В. С. ТИМОФЕЕВ, и М. И. БАЛАШОВ

В работе рассмотрены основные закономерности хода траекторий процесса ректификации при бесконечном флегмовом числе в аппаратах идеального противотока. Показано, что в этом случае области непрерывной ректификации характеризуются определенно уложенным в симплексе составов пучком траекторий процесса. Стационарные точки процесса ректификации являются узлами и седлами. Через эти точки проходят границы между областями ректификации, положение которых зависит от распределения между фазами сопротивления массопереносу. Характер укладки пучка траекторий в симплексе составов определяется струкутрой диаграммы фазового равновесия жидкость-пар. Проведена классификация областей ректификации. Исследован характер расположения зон постоянного состава в ректификационном аппарате идеального противотока.



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# SOME CHEMICAL REACTIONS OF THE ELECTRODE GAP AND THEIR ROLE IN SPECTROCHEMICAL ANALYSIS, X

## STUDY OF THE OXYGEN-NITROGEN REACTION

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## Received December 27, 1971

A procedure has been developed for the determination of nitrogen oxides produced in the arc. With this it has been shown that the primary product in the arc is nitrogen monoxide. Its amount, however, depends on the other reactions in the arc, and primarily on the formation of carbon dioxide; this reaction affects the local ratio of oxygen and nitrogen. The reaction zone of the oxygen and nitrogen increases almost linearly with the increase of the current.

In parts IV and V of this series an account was given of experiments with disc-shaped, rotated foundry aluminium samples in different oxygen-nitrogen mixtures [1], and in air with a varying current [2], with copper and carbon counter-electrodes. By means of gas chromatography in parallel with a spectral study, the oxygen consumption in the arc, depending on the polarity of the electrodes, and also, in the case of the carbon counter-electrode, the yield of carbon dioxide too were measured. It was pointed out that the oxygen consumption data not only refer to the reactions between the electrode materials and the oxygen in the gas atmosphere, but also include the amount of oxygen consumed in the oxygen-nitrogen reaction. The value of this, particularly in the case of the copper counter-electrode, when the total oxygen consumption of the arc is smaller, can clearly no longer be neglected. This reaction and energy requirement have been reviewed by Kocsis [3]. The effect exerted by the nitrogen oxide formed on the field-strength in the electric arc has been studied by KING [4]. MCCARTHY [5] has investigated the reaction in silent discharges in discharge tubes, while MALTSEV et al. [6-11] have made a detailed treatment of the stationary concentration of the nitrogen monoxide, its determination and its industrial importance. At reduced pressures (50-400 torr)they studied the dependence of the reaction on the current (50-700 mA), the suitable types of discharge tube, the role of the composition of the gas mixture, etc. The important role of nitrogen and oxygen atoms in the mechanism of the reaction has been pointed out [12]. The aim of the present work was to obtain further informations on the chemical reactions taking place in a polarized a.c. arc. It was planned to study how our earlier experimental data are affected by this reaction, and consequently how the shapes of the experimentally obtained graphs and the values of the individual points are modified. Measure-

ments were therefore carried out similarly as in our previous investigations, with oxygen-nitrogen mixtures of different ratios, and also in air with varying the current. A gas analysis procedure was developed for the determination of the nitrogen oxides formed in the arc: the nitrogen oxides are oxidized to nitric acid, which is titrated with a standard alkali solution.

## Experimental

The experiments were carried out with our customary, 6 mm thick and 20 mm diameter disc-shaped foundry aluminium electrodes, and an electrolytic copper or RW II carbon counter-electrode ending in a  $60^{\circ}$  frustum of cone. The electrode distance was 3 mm. Similarly as previously, the aluminium disc in the 50 cm<sup>3</sup> closed gas-cell rotation apparatus [13] was rotated during the investigation at a rate of 5 r.p.m. The cell was flushed out with a gas mixture of desired composition and then filled. In the case of the various oxygen-nitrogen mixtures the average current of the polarized a.c. arc was 12 A (the short-circuiting current in the entire period was 25 A), while in the runs where the current was varied air was used.

After an 8 sec burning the gas content of the cell was sucked into a  $dry 600 \text{ cm}^3$  reaction flask [14] evacuated previously with a water-pump, and was flushed with air, while the internal pressure was compensated by the external air pressure. The flask was allowed to stand for 15 min to enable the oxygen excess to convert the nitrogen monoxide completely to nitrogen dioxide. The closed flask was cooled with running water so that 4 ml 1% hydrogen peroxide (distilled and neutralized to methyl red) and 10 ml distilled water could be sucked into it. After standing for 1 hour, during which the contents of the flask were shaken at frequent intervals, the solution was flushed into a 200 cm<sup>3</sup> Erlenmeyer flask, pumice was added and the dissolved carbon dioxide was removed by boiling. After cooling the nitric acid formed, which was equivalent to the nitrogen oxide, was 'titrated with a 0.01 N sodium hydroxide solution in the presence of 1 drop of methyl red as indicator. 1 ml 0.01 N sodium hydroxide solution is equivalent to 0.224 cm<sup>3</sup> nitrogen dioxide in the standard state.

The procedure was checked by treating sodium nitrite solutions of known concentrations with potassium iodide under oxygen-free conditions to liberate nitrogen monoxide, which then was oxidized to nitric acid in a similar manner. The error of the measurement was always less than 1%.

## **Results and discussion**

Fig. 1 shows the amounts of nitrogen oxide, expressed as nitrogen dioxide, obtained by excitation with a *copper counter-electrode* in various oxygen-nitrogen gas mixtures. The points denoted by crosses and by triangles are the results of the anodic (a) and the cathodic (c) excitations, respectively, of the aluminium. The two curves coincide reasonably well. It is known that the reaction takes place mainly in the aureole and not on the surface of the electrode. Assuming that a definite isothermal layer of the plasma is the most favourable for the reaction, it emerges from the above that in the present case with a copper-aluminium electrode pair this isothermal surface and hence the volume of the plasma must be practically independent of the polarities of the electrodes.

The following data permit conclusions as to the zone with that temperature which is optimum for the reaction. Since nitrogen dioxide decomposes above 620°C to nitrogen monoxide and oxygen, and this reaction is reversible, the formation of the monoxide requires a temperature higher than this. Below 1500°C, however, the rate of formation of nitrogen monoxide is very low.

For this reason, temperatures higher even than this must be considered. According to literature data, at around  $3000^{\circ}$ C the reaction is rapid and leads to an equilibrium value of 5% [15]. In our case, however, there was no special effort to freeze the reaction, and since very different temperatures are to be found in the individual zones of the plasma, where the extent of reaction



Fig. 1. Measured amount of nitrogen oxide as a function of the oxygen content of the gas-cell (copper counter-electrode)

is shifted and the reaction may be reversed, this value is not attained. Nor can it be attained, because during the 8-sec burning time of the arc the total amount of gas (50 cm<sup>3</sup>) could not pass through the reaction zone of the arc plasma. Thus, even in the gas mixture with the optimum 50-50% composition a total of only 1.5% nitrogen monoxide was measured.

With a few simplifications it was possible to calculate the temperature at which the maximum amount of nitrogen monoxide is formed. Disregarding the small extent of ionization of the plasma gases because of the low temperatures involved, the most important equilibria which must be considered in the plasma are the following [17]:

The equilibrium constants are:

1\*

$$egin{aligned} K_{\mathrm{O}_2} &= rac{n_{\mathrm{O}_2}^2}{n_{\mathrm{O}_2}} \ K_{\mathrm{N}_2} &= rac{n_{\mathrm{N}}^2}{n_{\mathrm{N}_2}} \ K_{\mathrm{NO}} &= rac{n_{\mathrm{O}}\cdot n_{\mathrm{N}_2}}{n_{\mathrm{NO}}} \end{aligned}$$

where the n values have dimensions of numbers of particles per cm<sup>3</sup>. Ignoring the small amount (a few per cent) of the electrode material which enters the plasma, the total number of particles is given by

$$\Sigma_n = n_{
m O_2} + n_{
m O} + n_{
m N_2} + n_{
m N} + n_{
m NO} = 7.340 imes 10^{21} / T \; ,$$

where T is the absolute temperature.

The relative amounts of the individual particle species are also controlled by the initial ratio of the gases ( $O_2 : N_2$ ). For example, in the case of the initial gas composition  $20\% O_2 + 80\% N_2$  (1:4), the following relation holds:

 $4(n_{\text{O2}} + 1/2 n_{\text{O}} + 1/2 n_{\text{NO}}) = n_{\text{N2}} + 1/2 n_{\text{N}} + 1/2 n_{\text{NO}}.$ 

If the temperature is considered to be below 4500°C a further simplification is possible. The amount of the nitrogen atoms can be neglected here, because the dissociation of the nitrogen molecule begins practically above this temperature.

The mixed fourth-order equations obtained by reduction of the above equations were solved for the different temperatures and starting mixtures, using the data of ROES [16] and BOUMANS [17], and also the temperature dependence of the equilibrium constants:

$$\log K_n = A + 1/2 \log T + \log (1 - 10^{-0.625 \omega T}) - \frac{5040}{T} V_d$$

where A is a reduced physical constant (containing molecular and atomic weights, partition functions, statistical weights, and rotation constants),  $\omega$  is the vibrational constant, T is the absolute temperature, and  $V_d$  is the dissociation potential of the gas molecule in electron volts. For purposes of clarity, only a few of the results are given in Fig. 2. It can be seen from the graph that the curves attain their maxima at about  $3000-3200^{\circ}$ K, the highest temperature maximum belonging to the initial gas composition 50%  $O_2 + 50\%$   $N_2$ .

As was expected, the individual experimental points (Fig. 1) gave a symmetrical maximum curve, the maximum is found at a composition of 50% oxygen +50% nitrogen. This confirms that primarily nitrogen monoxide is formed in the arc, and that the two reaction partners arrive at the surface mentioned at approximately equal rates. The nitrogen monoxide next diffuses to the cooler regions, and later is transformed more slowly to nitrogen dioxide by the excess oxygen. If nitrogen dioxide were formed directly in a zone cooler than the previous one, then a maximum would appear on the curve at a gas mixture composition of about 67% oxygen and 33% nitrogen.

It could be shown from the data of the above calculation that this curve should be distorted because of the increasing dissociation of the oxygen (as

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Fig. 2. Calculated amounts of nitrogen monoxide in the plasma as a function of the temperature in the cases of some  $O_2 - N_2$  gas mixtures



Fig. 3. Measured (dashed line) and calculated (solid line) amounts of nitrogen monoxide as a function of the oxygen content of the cell

has been mentioned the dissociation of nitrogen is negligible in this temperature region). It also follows from the trend of the distortion of the curves that a decisive role is played in the main by the amount of oxygen molecules, and less by the amount of oxygen atoms, in the formation of the nitrogen monoxide. For the sake of better comparison, the curves were transformed to identical maximum values by the variation of the scales on the vertical axis of the graphs, and the experimentally measured data were fitted to these curves so that the maximum value agreed with that calculated (Fig. 3, in which only the values calculated for 1500 and 4500°K are shown in addition to the curves

obtained by measuring the data of the anodic and cathodic excitation of the aluminium). It can be seen that the cathodic curve for the aluminium exhibits a good agreement with that calculated for the lowest temperature. It must be concluded from this that, although the formation of nitrogen monoxide is faster at higher temperature (around  $3000^{\circ}$ K), during the diffusion to the cooler region of the plasma the equilibrium has time to adjust itself towards the values valid there, or possibly the greater part of the reaction nevertheless takes place in the lower-temperature zone. Due to the greater evaporation of the aluminium coupled as anode, its oxygen consumption is higher, too. A slight, but reproducible curve distortion is therefore observed. This may correspond to the fact that the same amount of oxygen is available for the reaction at somewhat higher oxygen percentages in the reaction zone.



Fig. 4. Measured amount of nitrogen oxide as a function of the oxygen content of the gas-cell (carbon counter-electrode)

Fig. 4 shows the results of the measurements with the carbon counterelectrode. The curves here are considerably distorted, the maxima being shifted towards higher oxygen percentages. In the case of anodic aluminium the maximum is at an oxygen content of about 60%, and in the cathodic case at about 70%. At the same time the height of the maximum is less, the anodic curve lying above the cathodic one. The reason for these phenomena is that the carbon electrode, as described earlier [1, 2], consumes a larger amount of oxygen and thus the composition of the gas atmosphere in a closed cell is appreciably changed. During the excitation the reaction takes place in an atmosphere increasingly poorer in oxygen. From the shift in the position of the maximum it is possible to make an approximate calculation of the total decrease in the oxygen content of the gas-cell during the burning of the arc. In the case of the anodically coupled carbon electrode this turned out to be 10 cm<sup>3</sup>, while in the cathodic case it was 5 cm<sup>3</sup>, in good agreement with the directly measured values. (For an oxygen content of 50%, Fig. 8 in part IV of this series [1] shows oxygen decreases of 10.0 and 4.6 cm<sup>3</sup>, the majority of

which is devoted to the formation of carbon dioxide.) This confirms, therefore, that the reason for the distortion of these curves is the oxygen consumption of the electrodes, which is greater when these are anodically excited. The height of the maximum decreases for the same reason.

In Fig. 4 in part IV of this series [1] (in the case of the *copper counter-electrode*) the consumption values relating to pure oxygen could not be given at that time because the gas chromatographic measurement did not give reliable results for these small values with the procedure based on the difference



Fig. 5. Total oxygen consumption of the arc as a function of the oxygen content of the gas-space (copper counter-electrode)



Fig. 6. Combined oxygen consumptions of the copper and aluminium electrodes as a function of the oxygen content of the gas-space

formation. It was pointed out in part VIII [18] that since those data referring to pure oxygen are common to the measurements in oxygen-argon and in oxygen-nitrogen mixtures, the missing values could be supplied by the titrimetric gas analysis data. The graphs so obtained are reported in Fig. 5 of the present paper, since they will be required later. This figure gives the data for the total oxygen consumption of the aluminium-copper electrode pair, and from these the amounts of oxygen consumed in the nitrogen-oxygen reaction can be subtracted. In this way Fig. 6 could be plotted; a and c indicate the polarities of the aluminium electrode. It is obvious also here that more oxygen is consumed by the more active aluminium anode, while the results are affected by the copper electrode to a much smaller extent. Even after the subtraction of the nitrogen dioxide values the curves did not become straight. The curves have a tendency to increase, and also exhibit maxima. The reason for the increase was given earlier [1]. The maximum nature follows the curve for the nitrogen oxide formation, suggesting that, proportionally with its amount, the nitrogen oxide increases the consumption of the electrode material, and hence its oxidation too. (Oxygen atoms are formed, in direct proportion to the

amount of nitrogen monoxide, as an intermediate in the chain reaction of the formation of nitrogen monoxide [12].) This effect is particularly significant with the anodic aluminium.

Curvature in the plots drawn from the similar difference values obtained with the *carbon counter-electrode* likewise remained; because of the large amount of carbon dioxide and the unknown amount of carbon monoxide, however, its



Fig. 7. Measured amount of nitrogen oxide as a function of the current (copper counter-electrode)



Fig. 8. Measured amount of nitrogen oxide as a function of the current (carbon counter-electrode)

nature cannot be established. For this reason the curves are not given here. We shall return to these data and curves in the future, when the direct data relating to the amount of carbon monoxide will be available.

The amounts of nitrogen oxides formed depend much less on the change of the current. Figs 7 and 8 show the data obtained with the copper and carbon counter-electrodes, respectively. In the case of the copper counter-electrode the curves obtained with the two types of polarity again agree well independently of the current. In each case the 3 experimental points (average values !) lie on a practically straight line, presumably as a resultant of two effects. Both the linearity and the approximate coincidence of the straight lines obtained with

the two types of polarity can be explained by the experimental fact that with increased evaporation the volume of the plasma increases, but its average temperature (deduced from the spectral character) decreases. In this way a reaction zone can develop, the temperature of which is optimal for the reaction, and which increases practically linearly with the increase of the current. In this zone the role of the lower evaporation in the case of the cathodic aluminium is counterbalanced by the higher average temperature of the arc compared to the anodic one. When a *carbon counter-electrode* is used, the differences arising from its oxygen consumption appear here too. The cathodic curve lies under the earlier common line and with increasing current, as the amount of oxygen consumed by the carbon also increases, the difference becomes larger.



Fig. 9. Combined oxygen consumptions of the copper and aluminium electrodes as a function of the current

A flatter curve is thus obtained. This difference is even greater in the case of the carbon anode, when, as has already been mentioned, the gas atmosphere becomes much poorer in oxygen. The curve attains the horizontal and it may be presumed that at even higher current (perhaps by means of the longer burning of the arc too) the experimental values will begin to decrease.

The above findings naturally refer to a closed gas-cell in which the gas supply is not secured. In our earlier experiments, however, it was shown that even in the case of a flowing gas the gas exchange by diffusion does not give complete mixing. Thus the oxygen consumption of the carbon electrode must influence the formation of nitrogen oxide in this case too.

Fig. 9 shows those curves which give the combined oxygen consumptions of the copper and aluminium electrodes as a function of the average current. These curves were obtained, similarly to those shown in Fig. 6, by subtracting the amounts devoted to the formation of nitrogen oxide from the total oxygen consumption of the arc [2]. The straight lines so obtained can be extrapolated to the origin. They confirm also that in the case of the copper-aluminium electrode pair the oxygen consumption of the aluminium is decisive, and that the oxidation of the aluminium begins even at very low current presumably mainly at the burning spot.

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# ANIONENAUSTAUSCHVERHALTEN VON URAN NEBEN ANDEREN METALLIONEN IM MIKROGRAMMBEREICH AM WOFATIT-SBU

## ANALYTISCHE ANWENDUNG VON ESSIG-, GLYKOL-, THIOGLYKOL-, BERNSTEIN-, ÄPFEL- UND THIOÄPFELSÄURE ALS KOMPLEXBILDNER

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Eingegangen am 10. Januar 1972

Es wurde das Ionenaustauschverhalten von Uran(VI) neben Thorium(IV) und anderen Metallionen im Mikrogrammbereich in Gegenwart von Essig-, Glykol-, Thioglykol-, Bernstein-, Äpfel- und Thioäpfelsäure bei verschiedenen pH-Werten untersucht und eine säulenchromatographische Trennung von Uran(VI) in Anwesenheit von Thioglykolsäure beschrieben. Außerdem wurden die Verteilungskoeffizienten von U(VI), Th(IV), Mo(VI), Fe(II), Fe(III), SE(III), Y(III), Mg(II), Ca(II), Sr(II) und Ba(II) bei pH-Werten von 2,5 und 4 in Gegenwart der angeführten Säuren im Batch- und Säulenverfahren am WOFATIT-SBU und -SBW bestimmt.

Während das Austauschverhalten von Uran(VI) an stark basischen Anionenaustauschern in Chlorwasserstoffsäure [1], Salpetersäure [2], Fluorwasserstoffsäure [3, 4] und Schwefelsäure [5] bzw. in verschiedenen Salzlösungen [6—9] systematisch untersucht wurde, gibt es — insbesondere an schwächer basischen Anionenaustauschern — nur wenige Arbeiten, in denen Komplexbildner zur säulenchromatographischen Abtrennung des Urans von Thorium und anderen Ionen herangezogen werden.

So untersuchten mehrere Autoren [10—15] das Austauschverhalten von Uran(VI) am Dowex-1, Amberlite-Ira-400 und Wofatit-M in acetathaltigen Lösungen und diskutierten die dafür in Frage kommenden negativ geladenen Uranyl-triacetato-, bzw. -tetraacetato-Komplexe. KORKISCH [16, 17] empfiehlt, zur Anreicherung von Uran(VI) am Amberlite-Ira-400 Ascorbinsäure als Komplexbildner zu verwenden. Li und WHITE [18], ZAKI und SHAKIR [19] sowie KORKISCH und HAZAN [20] beschreiben Trennmöglichkeiten des Urans von Thorium und anderen Elementen mittels gemessener Verteilungsverhältnisse am Dowex-1 bzw. Lewatit-MN in Gegenwart von aliphatischen Di- und Tricarbonsäuren bzw. Oxycarbonsäuren. CHEN [21] sowie ERISTAVI [22, 23] untersuchten die Sorption von Uran(VI)-EDTA-Komplexen am Amberlite-Ira-400 bzw. AN-2, AV-16, AV-17 und diskutierten einige Trennmöglichkeiten. JERCAN und DINOIN [24] versuchten schließlich mit Hilfe von Aminoessigsäure am Dowex-2 und Vionit-AT-1 Uran von anderen Ionen abzutrennen.

In der vorliegenden Arbeit wurde das Austauschverhalten des Urans(VI) in Gegenwart von Thorium und anderen Elementen am Anionenaustauscher Wofatit-SBU (und als Vergleich am Wofatit-SBW) in Anwesenheit von Essig- und Bernsteinsäure bzw. deren in  $\alpha$ -Stellung substituierten Derivaten untersucht.

## **Experimenteller** Teil

#### Trennsäulen und Harzvorbereitung

Die für die Trennversuche im Mikrogrammbereich verwendeten Trennsäulen hatten einen inneren Durchmesser von 5 mm und eine Länge von 300 mm. Es wurden stets 2 ml (ca. 200 mm Füllhöhe) vorgequollenen Harzes, mit einem ausgesiebten Korngrößenbereich von 0,1 bis 0,2 mm Durchmesser, eingesetzt. Als Anionenaustauscher dienten die in analysenreiner Form vom VEB CKB Bitterfeld-Wolfen hergestellten und in früheren Arbeiten auf ihr Austauschverhalten eingehend untersuchten Anionenaustauscher Wofatit-SBU [25] und Wofatit-SBW [26], die auf der Basis Polystyrol-Divinylbenzol aufgebaut sind. Beide Austauscher wurden vor Verwendung je dreimal in die Hydroxid- bzw. Chlorid-Form eingefahren und schließlich in der Chlorid-Form verwendet. Die Fließgeschwindigkeit betrug 0,5 bis 0,7 ml/min.

#### Lösungen und Reagenzien

Für die Standardlösungen wurden die analysenreinen Salze  $UO_2(NO_3)_2 \cdot 6H_2O$  und  $Th(NO_3)_4 \cdot 4H_2O$  (je 5 mg Metall/ml) verwendet. Als Störelemente wurden SE-Oxide (in HCl gelöst), Erdalkalichloride,  $Fe(NO_3)_3 \cdot 9H_2O$ ,  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$  und  $NH_4VO_3$  eingesetzt. Von den als Komplexbildner eingesetzten Verbindungen Essigsäure, Glykolsäure und Thioglykolsäure sowie Bernsteinsäure, Äpfelsäure und Thioäpfelsäure wurden ausschließlich 1M-Stammlösungen hergestellt.

Als Pufferlösung für die spektralphotometrische Uranbestimmung diente eine 1*M*-Chloressigsäurelösung, deren pH-Wert auf 3 durch Zusatz von 2*M*-NaOH und 8*M*-HCl eingestellt wurde.

Chlorpho<br/>sphonazo III wurde als 0,05%ige und Arsenazo III al<br/>s0,1%ige Lösung verwendet.

#### Quantitative Bestimmung der Elemente

Uran(VI) wurde spektralphotometrisch mit dem von Carl-Zeiss Jena hergestellten Spektralkolorimeter »Spekol« in 0,5 bis 1 cm Küvetten mittels Chlorphosphonazo III [27] und außerdem polarographisch [28] mit Hilfe des volltransistorisierten Squarewave-Polarographen OH-104 der Firma Radelkis, Budapest, bestimmt. Letzteres Gerät ist mit automatischer Tastzeitregelung ausgestattet und arbeitet mit 10, 20 und 40 mV/p.p. Für die Bestimmung von Thorium und der SE kam die photometrische Methode mittels Arsenazo III [29] bei pH 3 (SE) und in 4N-HCl (Thorium) am Spekol zur Anwendung.

Molybdän(VI) wurde durch Fällungstitration mit Bleinitratlösung bestimmt; der erste überschüssige Tropfen der Bleinitratlösung gibt mit PAR [4-(Pyridyl-2'-azo)-resorcin-natriumsalz] eine rote Färbung, außerdem gravimetrisch mit 8-Oxychinolin. Eisen(III) wurde im ammoniakalischen Medium in Gegenwart von Thioglykolsäure photometrisch bestimmt. Die Bestimmung der Erdalkalien und des Magnesiums erfolgte komplexometrisch mit Erio-T als Indikator.

#### Bestimmung der Durchbruchskapazität der Säulen

Zur Ermittlung der Durchbruchskapazität der eingesetzten Säulen wurde eine 0.1MThioglykolsäurelösung (pH = 2,5), die 100  $\mu$ g Uran/ml bzw. 100  $\mu$ g Thorium/ml enthielt, mit einer Durchflußgeschwindigkeit von 0,6 ml/min durch die Harzfüllung der Säule geschickt, die ablaufende Lösung in 5 ml Kölbchen aufgefangen und der Uran- bzw. Thoriumgehalt bestimmt. (Für Uran wurden 60 mg gemessen.)

#### Bestimmung der Verteilungskoeffizienten

Einige Verteilungskoeffizienten der Metallionen zwischen den Anionenaustauscherharzen und komplexen Lösungen wurden mittels des Säulenverfahrens (für die Seltenen Erden Lanthan, Samarium und für Yttrium) nach TOMPKINS und MAYER [30] bestimmt:

$$\overline{V} = D \cdot m$$

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In dieser Beziehung bedeuten D den Verteilungskoeffizient, m die Masse des trockenen Harzes in der Säule und V das Elutionsvolumen, abzüglich des Blindvolumens, bis zum maximalen Elutionspeak. Die übrigen D-Werte wurden nach der Batch-Methode ermittelt. Dabei werden in einem 25 ml Kölbchen jeweils 5 mg des entsprechenden Metallions in soviel ml Komplexbildnerlösung gelöst, daß damit Endkonzentrationen von 0,01-, 0,1-, 0,5- und 0,9-M an Komplexbildner erreicht werden. Dann wird der gewünschte pH-Wert durch Zugabe von NH<sub>3</sub> und HCl unter potentiometrischer Kontrolle eingestellt, je 0,25 g lufttrockenes Harz eingetragen und zum Eichstrich mit wenig H<sub>2</sub>O aufgefüllt. Nach 12stündigem Schütteln in einer Schüttelmaschine wird das Harz von der Lösung abgefrittet und die Metallionenkonzentration im Filtrat nach einer der oben angeführten Methoden bestimmt. Die experimentellen Fehler bei der Bestimmung von D liegen für kleine Werte bei  $\pm 5\%$  und bei Werten über 100 bei  $\pm 10\%$ .

## **Ergebnisse und Diskussion**

Nachdem in Vorversuchen festgestellt wurde, daß der Anionenaustauscher Wofatit-SBU die untersuchten Uranyl- und Thoriumionen in Gegenwart der angeführten Komplexbildner im pH-Bereich von 2-4 quantitativ sorbiert – bei größeren pH-Werten tritt infolge Hydrolyse Niederschlagsbildung auf – und in diesem Bereich die Erdalkali-, Seltenen Erdmetall-, Eisen(II)- und Eisen(III)-Ionen vom Harz nicht zurückgehalten werden, wurden die Verteilungskoeffizienten von Uran(VI) und Thorium(IV) in Anwesenheit von Essigsäure, Glykolsäure und Thioglykolsäure bei pH = 4 und in Anwesenheit von Bernsteinsäure, Äpfelsäure und Thioäpfelsäure bei pH = 2,5 im Batch-Verfahren bestimmt und die Gleichgewichts-Verteilungskoeffizienten nach der Beziehung

# $D = rac{\mu \mathrm{g \, Element/g \, luftrockenes \, Harz}}{\mu \mathrm{g \, Element/ml \, Lösung}}$

berechnet. In den Tabellen I und II sind die Ergebnisse angeführt.

Ion Komplexbildner (Mol/l)	Wofatit-SBU				Wofatit-SBW				
	0,01	0,1	0,5	0,9	0,01	0,1	0,5	0,9	
	Essigsäure	10	125	250	165	10	125	160	125
UO <sub>2</sub> (II)	Glykolsäure	220	575	425	150	575	315	190	100
Thioglykolsäure	1500	4000	2000	1100	1350	2500	2000	800	
	Essigsäure	15	125	25	10	15	10	15	15
Th(IV) Glykolsäure Thioglykolsäure	10	10	10	10	10	10	10	10	
	Flg.	Flg.	150	150	Flg.	Flg.	115	120	
									1

Tabelle IVerteilungskoeffizienten bei pH = 4 und 20° C

Aus den Tabellenwerten geht hervor, daß die Verteilungsverhältnisse von Uran(VI) und Thorium(IV) am Wofatit-SBU — und auch am stark basischen Anionenaustauscher Wofatit-SBW, der zum Vergleich in die Untersuchungen einbezogen wurde — am günstigsten in Gegenwart von Thioglykolsäure als Komplexbildner sind. Allerdings tritt bei pH = 4 teilweise

Ion Komplexbildner (Mol/l)	Komplexbildner		Wofatit-SBW				
	0,05	0,1	0,2	0,05	0,1	0,2	
	Bernsteinsäure	215	345	295	20	25	55
UO <sub>2</sub> (II) Äpfelsäure Thioäpfelsäure	1190	1565	2030	1850	1950	1380	
	Thioäpfelsäure	650	950	825	295	370	430
	Bernsteinsäure	20	40	10	20	25	20
Th(IV) Äpfelsäure Thioäpfelsäure	Äpfelsäure	470	425	330	615	435	445
	100	65	20	210	270	280	

Tabelle IIVerteilungskoeffizienten bei pH = 2,5 und 20° C

Niederschlagsbildung von Thorium auf, wodurch die Gefahr der Mitfällung von Uranylionen besteht. Aus diesem Grunde wurde zunächst der pH-Einfluß auf das Sorptionsverhalten des Wofatit-SBU gegenüber Uran, Thorium und einigen anderen als Störelemente bei der Trennung Uran von Thorium auftretenden Metallionen genau untersucht. Die Ergebnisse sind in Tabelle III eingeordnet. Die Tabellenwerte zeigen, daß in Gegenwart von 0,1 *M*-Thioglykolsäure sich als günstigster pH-Bereich der zwischen 2 und 2,5 für die Uran—Thorium-Trennung anbietet.

Wofatti-SBU in Anwesennett von Intoglykoisaure								
	рН	1	2	2,5	3	5	7	9
U(VI)	gegeb. (µg)	200	200	200	200	200	200	200
	gef. (µg)	4	196	202	199	200	201	204
Th(II)	gegeb. (µg)	200	200	200	200	200	-	200
	gef. $(\mu g)$	0	Spur	10	175	195	-	210
SE(III)	gegeb. (µg)	-	_	125	-	125	-	-
	gef. $(\mu g)$	-	-	20	-	15	-	-
Y(III)	gegeb. (µg)	-	-	125		125	-	_
	gef. $(\mu g)$	_		10		15	-	_
Mo(VI)	gegeb. (mg)	1,92		1,92	-	1,92	-	-
	gef. (mg)	1,90	_	1,85	_	1,80	-	
Fe(II),	gegeb. (mg)	1,12	-	1,12	1,12	1,12	1,12	1,12
(III)	gef. (mg)	0	-	0	0	Spur	1,14	1,14

Tabelle III pH-Einfluβ auf das Austauschverhalten von Uran(VI), Thorium(IV) u. a. Metallionen am Wofatit-SBU in Anwesenheit von Thioglykolsäure

Anschließend wurden die Verteilungsverhältnisse der genannten Metallionen in Gegenwart verschiedener Mengen Thioglykolsäure bei einem pH-Wert von 2,5 untersucht. Die ermittelten Verteilungskoeffizienten sind in Tabelle IV angeführt.

Ion		Wofatit-SBU Thioglykolsäure Mol/l				Wofatit-SBW			
	0,01	0,1	0,5	0,9	0,01	0,1	0,5	0,9	
UO <sub>2</sub> (II)	80	950	1050	800	20	125	320	750	
Th(IV)	15	25	40	45	5	15	25	45	
Mo(VI)	>103	$> 10^{3}$	$> 10^{3}$	$>10^{3}$	$>10^{3}$	$>10^{3}$	$>10^{3}$	>10	
Fe(II), (III)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	
SE(III)	< 1	3	5	10	< 1	3	5	5	
Y(III)	< 1	5	5	10	< 1	5	5	5	
Ca, Sr, Ba(II)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	
Mg(II)	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	
	-							1	

Tabelle IVVerteilungskoeffizienten bei pH = 2,5 und 20° C

Aus der Tabelle ist ersichtlich, daß die Trennmöglichkeit von Uran am Wofatit-SBU, von Thorium und anderen Störionen, bei pH = 2,5 in Anwesenheit von 0,1 bis 0,5 *M* Thioglykolsäure erfolgversprechend ist.

Die auf der Basis der ermittelten Verteilungsverhältnisse ausgearbeitete säulenchromatographische Trennung der Uranylionen von Thorium und anderen Störelementen in Anwesenheit von Thioglykolsäure am Wofatit-SBU ist in Abbildung 1 veranschaulicht. Die Elution erfolgt zunächst mittels



Abb. 1. Säulenchromatographische Trennung von 1000  $\mu$ g Th(IV) und 476  $\mu$ g U(VI) neben anderen in Tab. V angeführten Ionen bei 20° C. Säulenabmessung = 0,5 cm  $\emptyset$  und 2 ml Wofatit-SBU, Korngröße 0,1-0,2 mm  $\emptyset$ 

0,1 *M*-Thioglykolsäure, womit alle Erdalkali-, seltenen Erdmetall-, Eisen(II)-, Eisen(III)- und der Hauptanteil der vorhandenen Thoriumionen vom Austauscher eluiert werden. Nach ca. 100 ml Elutionslösung wird als Elutionsmittel 0,1 N-H<sub>2</sub>SO<sub>4</sub> eingesetzt, wobei die restlichen Thoriumionen im Eluat erscheinen. Im vorliegenden Versuch reichten dazu 50 ml 1N-H<sub>2</sub>SO<sub>4</sub> aus. Das noch am Harz zurückgehaltene Uran wird schließlich mit 1 *N*-HCl vollständig eluiert.

In Anwesenheit von Molybdän wird dieses nach der Abtrennung des Urans mittels einer ammoniakalischen Peroxydisulfatlösung nach ZIEGLER und RITTNER [31] vom Anionenaustauscher eluiert. In Tabelle V sind die nach

${{ m UO}_2({ m II})}\ { m gegeb.},\mu{ m g}$	Störelem gegeb.,	${f UO_3(II)}\ { m gef.,}\ \mu{ m g}$		
11 420	_	11 400		
19,5	-	-	19,5	
9,5	-		9,5	
476,0	Th(IV):	1 977	405,0	
380,8		100	380,0	
238,0		1 977	225,0	
238,0		1 977	240,0	
238,0		1 977	252,0	
190,5		100	190,0	
119,0		1 977	121,0	
38,0		400	38,0	
15,5		200	13,5	
15,5		2 000	18,5	
190,5	Mo(VI):	5 000	185,0	
190,5		5 000	190,0	
15,5		1 920	15,0	
15,5	Fe(II):	1 500	15,0	
15,5	Fe(III):	10 000	15 0	
15,5	SE(III):	850	17,5	
190,5		850	194,0	
15,5		850	20,0	
190,0		850	193,0	
119,0	Ca, Sr: j	$e  10^{-2} M$	120,0	
15,5	Ba, Mg: j	e $10^{-2}M$	16,0	

**Tabelle** V

Säulenchromatographische Trennung von Uran(VI) von anderen Ionen am Wofatit-SBU bei 20° C

dieser Trennmethode erzielten Ergebnisse in Gegenwart von Störionen in unterschiedlichen Mengenverhältnissen angeführt.

Aus den Meßwerten der Tabelle V ist zu sehen, daß der hier verwendete Ionenaustauscher Wofatit-SBU sehr gut geeignet ist für die Abtrennung der Uranylionen von Thorium und anderen Störionen, wenn die oben angeführten Bedingungen eingehalten werden. So können noch 10 ug Uran von einem 200fachen Thoriumüberschuß, von einem 500fachen Eisen-, 200fachen Molybdat-, 200fachen SE- und 500fachen Erdalkalien-Überschuß gut abgetrennt werden.

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## **RECTIFICATION OF MULTICOMPONENT** MIXTURES. III

## LOCAL CHARACTERISTICS OF THE TRAJECTORIES OF CONTINUOUS RECTIFICATION PROCESSES AT FINITE REFLUX RATIOS

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Local characteristics of rectification trajectories in the vicinity of steady-state points at finite reflux ratios are discussed. It is demonstrated that only "junction-type" and "saddle-type" steady-state points characterize the dynamic system of rectification. Different cases of the steady state in the system in question are analyzed. Ideal countercurrent models with the condition that the mass transfer coefficients for all constituents in both phases are identical were used in the analysis. For zeotropic mixtures with dia-grams in which no line  $\alpha_{ij} = 1$  is present, a general picture of the course of the trajec-tories for continuous rectification is given. The qualitative course of the steady-state lines in the concentration simplexes is demonstrated.

The fundamental local and non-local characteristics of rectification trajectories in concentration simplexes at infinite reflux ratio and finite or infinite column length were established previously [1].

The present paper deals with sets of conditions realizable at finite reflux ratios in apparatuses of infinite or finite length. An ideal liquid-vapour countercurrent model will be applied together with the condition that the partial mass transfer coefficients are identical for all constituents of the multicomponent mixture in both phases.

In the case when the resistance to mass transfer is distributed between the phases, the transferred mass of the ith constituent referred to 1 mole of the vapour phase  $(dq_i)$  can be expressed by the following equations:

$$dq_i = \frac{dy_i}{dl} = \beta_l^{(y)}(y_i^g - y_i); \qquad (1)$$

$$dq_i = \frac{mdx_i}{dl} = \beta_i^{(x)}(x_i - x_i^g) . \qquad (2)$$

where  $\beta_i^{(y)}$  and  $\beta_i^{(x)}$  — mass transfer coefficients of constituent *i* in the vapour and liquid phase, respectively;

 $y_i^g$  and  $x_i^g$  — interface concentrations of constituent *i* in the vapour

and liquid phase, respectively. It is assumed that these are equilibrium concentrations, i.e.  $y_i^g = K_i^g x_i^g$ , where  $K_{i}^{g}$  is the equilibrium distribution coefficient;

 $y_i$  and  $x_i$  — working concentrations in the interior of the vapour and liquid streams, respectively, related to each other in the general case by the material balance  $y_i = mx_i + (1 - m)x'_i$ ,

where m — slope of the working line,

 $x'_i$  — concentration of constituent *i* in the final fraction of rectification, *i.e.* concentration in the distillate (m < 1) or in the bottom product (m > 1).

The simultaneous solution of Eqs (1) and (2), with the elimination of  $dq_i$  yields

$$\beta_{i}^{(x)} x_{i} + \beta_{i}^{(y)} y_{i} = \beta_{i}^{(x)} x_{i}^{g} + \beta_{i}^{(y)} y_{i}^{g}.$$
(3)

Let us orient the segments  $y_i - x_i$  and  $y_i^g - x_i^g$  in the direction pointing from the liquid phase composition towards the vapour phase composition. We then obtain two vectors,  $\overrightarrow{x_i y_i}$  and  $\overrightarrow{x_i^g y_i^g}$ . The length and direction of the first vector will be determined by the working concentrations  $x_i$  and  $y_i$  of the liquid and vapour phases, respectively. The length and direction of the second vector coincide with the length and direction of the liquid-vapour node. Eq. (3) indicates that the intersection of the two vectors is at

$$x_i^0 = y_i^0 = \frac{\beta_i^{(x)} x_i + \beta_i^{(y)} y_i}{\beta_i^{(x)} + \beta_i^{(y)}} = \frac{\beta_i^{(x)} x_i^g + \beta_i^{(y)} y_i^g}{\beta_i^{(x)} + \beta_i^{(y)}} .$$
(4)

The intersection point  $x_i^0 = y_i^0$  divides both vectors into parts which are proportional to  $\beta_i^{(x)}$  and  $\beta_i^{(y)}$ . Thus the position of the point  $x_i^0 = y_i^0$  is determined by the relative distribution of the resistance to mass transfer between the liquid and vapour phases.

The vector  $\overrightarrow{y_i y_i^g}$  in Eq. (1), present as the driving force  $y_i^g - y_i$ , is defined as the difference of two vectors:

$$\overrightarrow{y_i}\overrightarrow{y_i^g} = \overrightarrow{x_i^0}\overrightarrow{y_i^g} - \overrightarrow{x_i^0}\overrightarrow{y_i} .$$
 (5)

Analogously, the vector  $\overrightarrow{x_i x_i^g}$  is also determined as the difference of two vectors:

$$\overrightarrow{x_i x_i^g} = \overrightarrow{x_i^0 x_i} - \overrightarrow{x_i^0 x_i^g}.$$
 (6)

At the same time, the equalities

$$|x_i^0 x_i^g| + |x_i^0 y_i^g| = |x_i^g y_i^g|$$
(7)

and

$$|x_i^0 x_i| + |x_i^0 y_i| = |x_i y_i|$$
(8)

are valid.

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#### SERAFIMOV et al.: RECTIFICATION OF MULTICOMPONENT MIXTURES, III

The working concentrations are connected through the material balance equation

$$y_i = mx_i + (1 - m) x'_i$$

and, consequently,  $dy_i = m dx_i$ .

Analogous equations can be written for any other constituent of the multicomponent mixture. By dividing one by the other, the equation

$$\frac{dy_i}{dy_i} = \frac{dx_i}{dx_i} \tag{9}$$

will be obtained for any pair of constituents. It follows from Eq. (9) that the tangents to the trajectories of the process relative to the liquid and vapour phases will be parallel lines in the composition simplex.



Fig. 1. Different formulations of driving force in the rectification process. a — Resistance to mass transfer concentrated in the vapour phase; b — resistance to mass transfer distributed between the phases; c — resistance to mass transfer concentrated in the liquid phase; D — point corresponding to the distillate; G — trajectory of the vapour phase; L — trajectory of the liquid phase

In view of Eqs (5) and (6), it can be seen that these tangents correspond to the vectors  $\overrightarrow{y_i y_i^g}$  and  $\overrightarrow{x_i x_i^g}$  and these vectors are collinear.

The results obtained are illustrated by Fig. 1b where the trajectories of the process for the concentrating part of the column (m < 1) are presented.

If the resistance to mass transfer is concentrated in the vapour phase,  $x_i = x_i^0 = x_i^g$  and  $y_i^g = y_i^*$ , where  $y_i^* = K_i^* x_i$  and  $K_i^*$  is the coefficient of equilibrium distribution (cf. Fig. 1a). If the resistance to mass transfer is concentrated in the liquid phase, obviously  $y_i = y_i^0 = y_i^g$  and  $x_i^g = x_i^*$ , where  $x_i^* = y_i/K_i^*$  (cf. Fig. 1c). In the following, the general case corresponding to the distribution of the resistance to mass transfer between the vapour and liquid phases will be discussed.

It follows from the material balance that when  $x_i = x'_i$  then  $y_i = x'_i$ . Let us determine the initial characteristics of the trajectories in their intersection points where  $x_i = y_i = x'_i$ .

Eq. (3) indicates that in the point in question  $x_i^0 = x_i = y_i$ , consequently,

$$dq_i = \frac{dy_i}{dl} = \beta_i^{(y)} (y_i^g - x_i^0)$$

$$dq_i = \frac{mdx_i}{dl} = \beta_i^{(x)} (x_i^0 - x_i^g).$$
(10)

Since the point  $x_i^0$  lies on the node  $\overline{x^g y^g}$ , both trajectories are tangential to this node in point  $x_i^0$ .

In fact, since  $\beta_i^{(y)}(y_i^g - x_i^0) = \beta_i^{(x)}(x_i^0 - x_i^g)$ , the following equations are obtained for any pair of constituents:

$$\frac{dy_i}{dy_1} = \frac{\beta_i^{(y)}(y_i^g - x_i^0)}{\beta_i^{(y)}(y_i^g - x_i^0)} = \frac{(y_i^g - x_i^0)}{(y_i^g - x_i^0)}$$
(11)

$$\frac{dx_i}{dy_j} = \frac{\beta_i^{(x)}(x_i^0 - x_i^g)}{\beta_j(x_j^0 - x_j^g)} = \frac{(x_i^0 - x_i^g)}{(x_j^0 - x_j^g)} .$$
(12)

If the resistance to mass transfer in the liquid phase is zero, obviously  $x_i = x_i^0 = x_i^g$  and, consequently, the tangent to both trajectories is the liquid vapour node  $\overrightarrow{x_i y_i^*}$ .

If the resistance to mass transfer in the vapour phase is zero,  $y_i = x_i^0 = y_i^g$  and, consequently, the vapour-liquid node  $y_i x_i^*$  is tangential to both trajectories.

The investigated cases of the positions of the trajectories and tangents are shown in Fig. 2. From this figure and from Eqs (11) and (12) it can be seen that the trajectories of the process in the liquid and vapour phases are tangential to each other in the points that correspond to the compositions of the final fractions of rectification, *i.e.* to the fractions corresponding to the compositions of the bottom product and of the distillate, respectively.

Let us now assume that for one of the constituents  $y_i = y_i^g$ . Then, in Eq. (1),  $dy_i/dl = 0$ , and, since the above vectors are parallel,  $x_i = x_i^g$  and  $dx_i/dl = 0$ . This result corresponds to the condition of extreme values on the trajectories with respect to the concentration of constituent *i*. Under these conditions the vectors  $\overrightarrow{y_i y_i^g}$  and  $\overrightarrow{x_i x_i^g}$  will become parallel to the hyperboundary

of the concentration simplex corresponding to an (n-1)-constituent mixture from which constituent i is absent.

Thus, the extrema with respect to concentration on the rectification trajectories corresponding to the liquid and vapour phase will be observed at one and the same point of the rectification column. In addition, the type of the extremum (maximum or minimum) will be identical on both trajectories.



Fig. 2. Positions of the trajectories and the liquid-vapour nodes in the vicinity of the distillate point. Resistance to mass transfer: a) concentrated in the vapour phase; b) distributed between the phases; c) concentrated in the liquid phase

Let us now investigate the local characteristics of the trajectories in the vicinity of steady-state points. For this purpose, Eqs (1) and (2) will be combined, yielding the equations

$$\frac{dy_i}{dl} = \beta_i \left[ \left( y_i^g - x_i^g \right) - \left( y_i - x_i \right) \right]$$
(13)

for the trajectory of the vapour phase, and

$$\frac{dx_i}{dl} = \frac{\beta_i}{m} \left[ (y_i^g - x_i^g) - (y_i - x_i) \right]$$
(14)

for the trajectory of the liquid phase, where

$$\frac{1}{\beta_i} = \frac{1}{\beta_i^{(\mathbf{x})}} + \frac{1}{\beta_i^{(\mathbf{y})}}$$

The steady-state points of the trajectories occur when the right sides of Eqs (13) and (14) take the value of zero. It can be readily seen that the right sides of Eqs (13) and (14) turn to zero simultaneously, since  $\beta_i \neq 0$  and the differences in brackets are identical in both equations. Evidently, the condition of steady state is expressed by the system of equations

 $\begin{array}{l} (y_1^q - x_1^g) - (y_1 - x_1) = 0 \\ (y_2^q - x_2^g) - (y_2 - x_2) = 0 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ (y_{n-1}^g - x_{n-1}^g) - (y_{n-1} - x_{n-1}) = 0. \end{array}$ (15)

Let us assume that  $y_i = x_i$  in all equations of the system (15). This means that the compositions of both the liquid and vapour phases are identical with that of a final fraction of rectification, *i.e.* the bottom product (m > 1) or distillate (m < 1).

Then the equalities  $y_i^g = x_i^g$  will correspond to the condition of steady state. These equalities indicate that the compositions of the vapour and liquid phases are identical and, consequently, the steady-state point will correspond to the pure constituent or to an azeotropic mixture containing two to *n* constituents.

Thus, if the steady-state point coincides with the point corresponding to the distillate or bottom product, then this steady-state point of the rectification trajectory will correspond to a singular point on the liquid-vapour equilibrium phase diagram. The results fully correspond to the steady-state set of conditions at infinite reflux ratios (m = 1) set forth earlier [1]. It should be remarked that the condition of all differences  $y_i^g - x_i^g$  simultaneously changing to zero at  $y_i \neq x_i$  does not in itself lead to the conditions of the steady state and cannot be realized in practice. In this case, if a trajectory would pass through a singular point (e.g. the point corresponding to the *n*constituent azeotropic mixture) at a finite velocity, without any interference source, a temperature extremum would be observed along this trajectory, contradicting the second law of thermodynamics.

The conditions of the steady state in the investigated case will be called external conditions of the steady state, since the compositions corresponding to the steady-state points are identical in this case with the compositions of the final fractions, *i.e.* the distillate or the bottom product.

The second condition of the steady state is the equality  $y_i^g - x_i^g = y_i - x_i$  for all constituents. These equalities occur at  $y_i^g = y_i$  and  $x_i^g = x_i$  (cf. Eqs 1 and 2). In this case, the vectors  $\overrightarrow{x_i y_i}$  and  $\overrightarrow{x_i^g y_i^g}$  coincide and con-

sequently the length of the vectors  $\overrightarrow{y_i y_i^g}$  and  $\overrightarrow{x_i x_i^g}$  becomes zero and their direction indeterminate.

The above case of the steady state is illustrated in Fig. 3.

It can readily be seen that in this case  $y_i = y_i^g = y_i^*$  and  $x_i = x_i^g = x_i^*$ and consequently, the resistance to mass transfer is equal to zero in both phases. This condition of the steady state will be called internal condition since it is fulfilled in a given zone of the rectification apparatus and the composition in this zone is not the same as that of the final products of rectification.



Fig. 3. Relative position of the rectification trajectories and the liquid-vapour nodes corresponding to the internal conditions of the steady state. a – Concentrating part of the column; b – exhausting part of the column; D – point of distillate; W – point of bottom product

For our further investigation, Eqs (13) and (14) are rearranged, taking into account Eq. (3), to give

for the vapour phase, and

for the liquid phase, where

$$\frac{1}{B_i} = \frac{K_i^g}{\beta_i^{(x)}} + \frac{1}{\beta_i^{(y)}}$$

and consequently,  $B_1 \neq B_2 \neq \ldots \neq B_{n-1}$  since  $K_1^g \neq K_2^g \neq \ldots \neq K_{n-1}^g$ .

As each steady-state point in the diagram of the trajectories described by Eqs (16) has a corresponding steady-state point in the diagram of the trajectories described by Eqs (17), we shall limit our further investigations to the system of equations (17). Taking into account that  $y_i = mx_i + (1 - m)x'_i$ , Eqs (17) can be further rearranged by substituting  $y_i$ .

The following equations are obtained [2]:

Let us assume that the steady-state point corresponds to the composition  $x_i^{(2)}$ . We then shift the origin of the coordinates to the singular point in question by introducing the variable  $\zeta_i = x_i - x_i^{(2)}$ . Thereby Eqs (18) will take the form

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By expanding the value  $(K_i^g - m)$  into a Taylor series with respect to variables  $x_1, x_2$ , etc., and retaining only the linear terms, we obtain

The type of the investigated steady-state point will depend on the signs of the roots of the characteristic equation established by means of the determinant of Eqs (20):

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 $\partial x_i$ 

 $\partial x_i$ 

acteristic equation (21) can be written in the following form:

$$\begin{vmatrix} \left(\frac{\partial y_1^*}{\partial x_1} - m\right) - \lambda & \frac{\partial y_1^*}{\partial x_2} \dots & \frac{\partial y_1^*}{\partial x_{n-1}} \\ \frac{\partial y_2^*}{\partial x_1} & \left(\frac{\partial y_2^*}{\partial x_2} - m\right) - \lambda \dots & \frac{\partial y_2^*}{\partial x_{n-1}} \\ \dots & \dots & \dots & \dots & \dots \\ \frac{\partial y_{n-1}^*}{\partial x_1} & \frac{\partial y_{n-1}^*}{\partial x_2} \dots & \left(\frac{\partial y_{n-1}^*}{\partial x_{n-1}} - m\right) - \lambda \end{vmatrix} = 0.$$
(22)

Let us add and subtract 1 to each diagonal term and designate the term  $(\lambda + m - 1)$  by  $\lambda_0$ ; the following form of the characteristic equation is obtained:

$$\begin{vmatrix} \left(\frac{\partial y_1^*}{\partial x_1} - 1\right) - \lambda_0 & \frac{\partial y_1^*}{\partial x_2} \dots & \frac{\partial y_1^*}{\partial x_{n-1}} \\ \frac{\partial y_2^*}{\partial x_1} & \left(\frac{\partial y_2^*}{\partial x_2} - 1\right) - \lambda_0 \dots & \frac{\partial y_2^*}{\partial x_{n-1}} \\ \dots & \dots & \dots & \dots & \dots \\ \frac{\partial y_{n-1}^*}{\partial x_1} & \frac{\partial y_{n-1}^*}{\partial x_2} \dots & \left(\frac{\partial y_{n-1}^*}{\partial x_{n-1}} - 1\right) - \lambda_0 \end{vmatrix} = 0.$$
(23)

The characteristic equation (23) corresponds to the dynamic system of free equilibrium evaporation and characterizes the course of distillation trajectories in the vicinity of singular points. A study of this equation indicated that all its characteristic roots  $\lambda_0$  are real [3].

Since  $\lambda = \lambda_0 + 1 - m$ , the roots of the characteristic equation (22) will also be real, indicating that the steady-state points of the equation system (18) are either junctions (all  $\lambda$  values have the same sign) or saddles (some of the  $\lambda$  values are positive, while others are negative).

The presence of focuses and centres is excluded.

Let us now investigate the case where the steady-state point in question is a singular point in the liquid-vapour phase equilibrium diagram.

Since  $x_i = y_i = x'_i = x^g_i$ , the signs and values of the roots of the characteristic equation (22) will fully coincide with those of the characteristic equation for the dynamic system of free evaporation. This means that *n*-constituent azeotropic mixtures with minimum or maximum boiling temperatures will correspond to junction steady-state points on the diagram of rectification

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trajectories. Hyperbolic *n*-constituent azeotropic mixtures will correspond to steady-state points of the "saddle" type. Naturally the azeotropic mixture with the minimum boiling point can be removed as distillate and the azeotropic mixture with the maximum boiling point as bottom product. The azeotropic mixture of the saddle type can be removed both as distillate and as bottom product, depending on which of the separatrixes passing through the steady-state point determines the course of the rectification process.

As for azeotropic mixtures containing (n-1), (n-2), etc., constituents, if they appear as junctions in the trajectory diagram, then the azeotropic mixtures with minimum boiling temperatures will be removed in the distillate and those with maximum boiling temperatures in the bottom product. If they appear as saddles in the trajectory diagram, the azeotropic mixture with the maximum boiling temperature can be removed in the distillate and that with the minimum boiling point in the bottom product. Naturally, in the case of steady-state points of the saddle type, only one of the trajectories, the one which passes through these steady-state points, will have a physical meaning.

As demonstrated in Refs [4, 5], some of the azeotropic mixtures containing (n-1) constituents may appear as steady-state points that are composite with respect to the boundary of the concentration simplex consisting of its hyperboundary, edges and vertexes. Points of the positive-negative junction, saddle-junction and positive-negative saddle type are such steadystate points. If an n-constituent mixture is being separated in the column, azeotropic mixtures of this type cannot be removed either as distillates or as bottom products. For instance, the point corresponding to the constituent with medium volatility in ternary mixtures is a point of this type. With respect to the Gibbs triangle, this point is a positive-negative junction and consequently it is impossible to separate the constituent with medium volatility by rectification at any finite value of m. The generalized situation may be formulated as follows: only those constituents can be removed in the form of final products in continuous rectification to which steady-state points of the "junction" type correspond in the vertexes of the concentration simplex. The vicinities of the steady-state points discussed above are segments of saddles of different orders and, therefore, not a single trajectory of the rectification process from the interior of the concentration simplex passes through these points.

The cases discussed above are related to the external conditions of the steady state. As for the internal conditions of the steady state, they appear each time when the direction of the liquid-vapour nodes in the concentration simplex coincides with the direction of the lines uniting the points corresponding to the final product composition and to the actual composition in the interior of the column (cf. Fig. 3).

It is known from the theory of equilibrium distillation and equilibrium condensation that the liquid-vapour and vapour-liquid nodes are tangential to these trajectories [6]. If a series of lines are traced from the distillate point or the bottom product point and all tangential points of these lines to the trajectories of equilibrium distillation and equilibrium condensation are determined, it is possible to find two limiting multitudes of the interior steady-



Fig. 4. Steady-state lines in the diagrams of zeotropic mixtures at different numbers of zero concentrations in the final products of the rectification.  $a \ b \ c$  – Concentrating part of the column; a'b'c' – exhausting part of the column;  $a \ a'$  – no zero concentrations;  $b \ b'$  – one zero concentration;  $c \ c'$  – two zero concentrations

state points. One of these corresponds to the conditions under which the resistance to mass transfer is concentrated in the vapour phase, the other to those where the resistance is concentrated in the liquid phase.

Each pair of points corresponds to a definite value of m. Both multitudes limit a definite set of compositions in the interior of the concentration simplex which corresponds to the intermediate cases of resistance to mass transfer distribution between the phases.

In Fig. 4 an example is given for the construction of the multiplicities of interior steady-state points for the case of ternary azeotropic mixtures in which the resistance to mass transfer is distributed between the phases. The first three diagrams correspond to the case of the concentrating part of the column under the conditions that all constituents are present in the distillate (Fig. 4a), two constituents are present (Fig. 4b) and one constituent is present (Fig. 4c). The second series of diagrams (Figs 4a', 4b' and 4c') is related to the

exhausting part of the column. It should be mentioned that in the case of azeotropic mixture, when two zero-concentrations are present in the distillate or in the bottom product, and not a single line is present in the Gibbs triangle along which the relative volatility  $\alpha_{ij}$  of the constituents *i* and *j* (having zero concentrations) is equal to 1, the line of the steady-state points breaks down into two branches proceeding along the sides of the Gibbs triangle (Figs 4c and 4c'). Also, two values of *m* correspond to one and the same distillate point (Fig. 4c) or bottom product point (Fig. 4c'), which are the limiting values of *m* in the binary systems 1—2 and 1—3, resp.



Fig. 5. Steady-state lines in the diagrams of zeotropic mixtures with two zero concentrations in the final products. A line  $\alpha_{ij} = 1$  exists. a – Concentrating part of the column; b – exhausting part of the column

For the distillate (Fig. 4c)

$$m_{12} = \lim_{x_2 \to 0} \frac{dy_1^*}{dx_1}, \quad m_{13} = \lim_{x_3 \to 0} \frac{dy_1^*}{dx_1}$$

For the bottom product (Fig. 4c')

$$m_{13} = \lim_{x_1 \to 0} \frac{dy_1^*}{dx_1}, \quad m_{32} = \lim_{x_2 \to 0} \frac{dy_2^*}{dx_2}.$$

The case where two constituents *i* and *j* have zero concentration in the final product, while the line  $\alpha_{ij} = 1$  passes in the interior of the Gibbs triangle, is of particular interest. In this case the line of the steady-state points coincides with the line  $\alpha_{ij} = 1$ . Fig. 5 demonstrates a similar case which can be encountered in zeotropic mixtures. Here the line of the steady-state points has three branches. Their intersections form a curved triangle.

Naturally, each steady-state point of the branches corresponds to a definite value of m, *i.e.* to a definite ratio of the liquid and vapour streams in the column, and can be of the junction or saddle type with respect to the recti-

fication trajectories, depending on the signs of the characteristic roots of Eq. (22).

The thermodynamic-topological analysis reveals different cases for the course of multitudes  $\alpha_{ij} = 1$  in the concentration simplexes. Since several fundamentally differing variants of the course of the multiplicities  $\alpha_{ij} = 1$  correspond to each class and type of diagram, the total number of the possible cases sharply increases with the number of constituents, being as high as 135 already in ternary mixtures.

Let us examine in some detail the local characteristics of the course of the trajectories in the vicinity of steady-state points, taking into account the internal conditions of steady state. Ternary mixtures shall be discussed by way of example.

## 1) The distillate or the bottom product contains all the constituents

After rearrangement, the conditions of steady state (Eq. 15) for the liquid phase can be written in the form

$$\begin{aligned} x_{1}^{(z)} &= \frac{1-m}{K_{1}^{g}-m} x_{1}^{\prime} \\ x_{2}^{(z)} &= \frac{1-m}{K_{2}^{g}-m} x_{2}^{\prime} \\ x_{3}^{(z)} &= \frac{1-m}{K_{3}^{g}-m} x_{3}^{\prime} \end{aligned}$$
(24)

where  $x_1^{(z)}$ ,  $x_2^{(z)}$  and  $x_3^{(z)}$  are the concentrations of the constituents corresponding to the internal conditions of the steady state, *i.e.* the coordinates of the steadystate points. The type of the steady-state point is determined by the signs of the roots of characteristic equation (22) which — for the ternary mixture — has the following form:

$$\begin{vmatrix} \frac{\partial y_1^*}{\partial x_1} - m \end{pmatrix} - \lambda & \frac{\partial y_1^*}{\partial x_2} \\ \frac{\partial y_2^*}{\partial x_1} & \left( \frac{\partial y_2^*}{\partial x_2} - m \right) - \lambda \end{vmatrix} = 0.$$
 (25)

If  $\partial y_1^*/\partial x_1 < 0$  and  $\partial y_2^*/\partial x_2 < 0$ , the steady-state point will be an unstable junction. If the conditions  $0 < \partial y_1^*/\partial x_1 < m$  and  $0 < \partial y_2^*/\partial x_2 < m$  are fulfilled, the investigated steady-state point will also be an unstable junction. If the inequalities  $0 < m < \partial y_1^*/\partial x_1$  and  $0 < m < \partial y_2^*/\partial x_2$  are fulfilled, the investigated steady-state point will be a stable junction.

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Finally, if for one constituent the inequality  $0 < m < \partial y_1^*/\partial x_1$  and for the other constituent  $0 < \partial y_2^*/\partial x_2 < m$  or  $\partial y_2^*/\partial x_2 < 0$  will be fulfilled, the steady-state point will be of the saddle type. Since the set of the possible steady-state points forms a line in the Gibbs triangle (cf. Figs 4a, 4a'), and each point of this line corresponds to a definite value of m, under the chosen conditions there will be not more than one steady-state point in the interior of the Gibbs triangle for the case of a zeotropic mixture at any optional value of m. Thus, in the presence of all three constituents in the distillate or in the bottom product, for zeotropic mixtures the equation system (24) will always have one solution with positive values of  $x_1^{(2)}$ ,  $x_2^{(2)}$  and  $x_3^{(2)}$ . If in this case the line  $\alpha_{23} = 1$  is absent, the steady-state point in question will be of the junction type.

## 2) The concentration of the constituents in the final product is zero

In this case the condition of the steady state can be written, for example, n the following form:

$$\begin{aligned} x_1^{(z)} &= \frac{1-m}{K_1^g - m} x_1' \\ x_2^{(z)} &= \frac{1-m}{K_2^g - m} x_2' \\ (K_3^g - m) x_3^{(z)} &= 0. \end{aligned}$$
(26)

Since the independent variables in this system of equations are the concentrations of any two constituents, one of the steady-state cases will correspond to

$$\begin{aligned} x_1^{(z)} &= \frac{1-m}{K_1^g - m} \, x_1' \\ x_3^{(z)} &= 0 \,. \end{aligned}$$
 (27)

In this case, the steady-state point is located on the 1-2 side of the Gibbs triangle. Then, characteristic equation (22) will have the form

$$\left[\left(\frac{\partial y_1^*}{\partial x_1} - m\right) - \lambda_1\right]. [(K_3^g - m) - \lambda_3] = 0.$$
(28)

From this equation, the explicit form of the characteristic roots  $\lambda_1$  and  $\lambda_3$  can be obtained:

$$\lambda_1 = \frac{\partial y_1^*}{\partial x_1} - m , \quad \lambda_3 = K_3^g - m.$$
<sup>(29)</sup>

In the concentrating part of the column, the derivative  $\partial y_1^*/\partial x_1$  for the binary combination 1—2 is always greater than m, consequently,  $\lambda_1$  is always positive. As for the limiting value of the distribution coefficient of the third constituent at  $x_3 \rightarrow 0$ , for zeotropic mixtures this is always lower than m. Consequently, the steady-state point corresponding to the condition  $x_3 = 0$  will be of the saddle type for zeotropic mixtures.

In the general case, the following variants are possible for azeotropic mixtures:

Another steady-state condition corresponding to Eq. (26) is

$$x_1 = \frac{1-m}{K_1^g - m} x_1', \quad K_3^g = m .$$
(30)

In this case the steady-state point is located in the interior of the Gibbs triangle. Consequently, in accordance with the choice of the independent concentrations, and taking into account that  $K_3 - m = 0$ , characteristic equation (22) will have the following form:

$$\begin{vmatrix} \left(\frac{\partial y_1^*}{\partial x_1} - m\right) - \lambda & \frac{\partial y_1^*}{\partial x_2} \\ \frac{\partial y_2^*}{\partial x_1} & x_3^{(z)} & \frac{\partial K_3^g}{\partial x_2} - \lambda \end{vmatrix} = 0 .$$
(31)

Theoretically, various combinations of the signs of the characteristic roots are possible for Eq. (31), similarly as for Eqs (22) and (25). For the specific case of zeotropic mixtures, the steady-state point will be of the junction type  $(\lambda_1 \ \lambda_2 > 0)$ .

3) The final product of the continuous rectification is a pure constituent, while the other two constituents have zero concentrations

In this case, choosing the concentrations of the zero-concentration constituents as independent variables and taking into account that  $x'_1 = 1$ , two conditions for the steady state will be obtained from Eq. (24):

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$$x_1^{(2)} = \frac{1-m}{K_1^g - m}, \quad K_2^g = m, \quad x_3^{(2)} = 0$$
 (32)

$$x_1^{(z)} = \frac{1-m}{K_1^g - m}, \quad K_3^g = m, \quad x_2^{(z)} = 0.$$
 (33)

Condition (32) corresponds to the location of the steady-state point on the 1-2 side of the Gibbs triangle, the condition (33) to its location on side 1-3.

From the characteristic equation fulfilling conditions (32) and (33), the roots can be obtained in the explicit form:

$$\lambda_1 = \frac{\partial y_1^*}{\partial x_1} - m \qquad \lambda_3 = K_3^g - m \qquad (32a)$$

$$\lambda_1 = rac{\partial y_1^*}{\partial x_1} - m \qquad \lambda_2 = K_2^g - m.$$
 (33a)

The type of the steady-state points depends on the signs of roots  $\lambda_1$ ,  $\lambda_3$  and  $\lambda_1$ ,  $\lambda_2$ .

If no line  $\alpha_{23} = 1$  is present in the Gibbs triangle, then  $K_2^g \neq K_3^g$  and the interior of the triangle does not contain a steady-state point. If, on the other hand, a line  $\alpha_{23} = 1$  exists, it is possible that in addition to the steadystate points located on the sides of the Gibbs triangle, steady-state points also appear in its interior. The condition of the steady state corresponding to this case can be written in the form

$$x_1^{(z)} = \frac{1-m}{K_1^g - m}$$
(34)  
$$K_2^g = K_3^g - m.$$

The above analysis refers to trajectories characterizing the change of concentrations in the liquid phase along the height of the column. An analogous analysis can also be carried out for trajectories characterizing concentration changes in the vapour phase.

It has been mentioned that to each steady-state point in the liquid phase trajectory diagram (1), a steady-state point of the same type corresponds in the vapour phase trajectory diagram (2). This means that any trajectory diagram (1) may be continuously and unequivocally transformed into diagram (2), *i.e.* correspondence exists between these diagrams. The transformation function can be written in the form  $f: X \to Y$ , where  $x_i \in X$  and  $y_i \in Y$ . This transformation is essentially different from the mutual transformation of the diagrams referring to free evaporation and free condensation. In the latter case, all steady-state points in the diagrams remained immobile during

the transformation. These were points corresponding to azeotropic mixtures of different orders and points corresponding to the pure constituents. When the trajectory diagrams of continuous rectification (1) and (2) are mutually transformed, only those steady-state points remain immobile that correspond to the external conditions of the steady state, *viz.* the compositions of the final products correspond to azeotropic mixtures or to pure constituents. As for the steady-state points corresponding to internal conditions of the steady state, they are not immobile, but are shifted by the transformation along with the liquid-vapour nodes.

Let us now consider some non-local characteristics of the trajectory diagram of continuous rectification.

Since the trajectories of the liquid (1) and of the vapour (2) are in unequivocal correspondence, the analysis will be performed with trajectories (1). The simplest case is that of zero class diagrams [7], including, in particular, diagrams of ideal mixtures and of mixtures containing no azeotropic mixtures. In the case of such diagrams, the total area of the Gibbs triangle corresponds to one rectification range [8]. The course of the trajectories in diagrams of this type is presented in Fig. 6. Figs 6a, 6b and 6c correspond to m < 1 (concentrating part of the column), while Figs 6a', 6b' and 6c' correspond to m > 1 (exhausting part of the column). All diagrams are characterized by three steady-state points whose relative position determines the presence or absence of zero constituents in the final products. In diagrams 6a and 6a', corresponding to the case that all constituents are absent in the distillate (Fig. 6a) or in the bottom product (Fig. 6a'), one steady-state point is found in the interior of the Gibbs triangle, this point being of the stable junction (type  $N_F$  in Fig. 6a) and of the unstable junction type ( $N_F$  in Fig. 6a'), respectively. Outside the Gibbs triangle, each diagram contains one junction  $(N_D \text{ and } N_W)$  and one saddle  $(C_F \text{ and } C_W)$ . Naturally, in both diagrams only the one trajectory which passes through point D corresponding to the composition of the distillate or through point W corresponding to the composition of the bottom product has any physical meaning.

Figs 6b and 6b' represent the cases where the concentration of one constituent is zero in the distillate (6b) or in the bottom product (6b').

By passing to this set of conditions, the junction-type steady-state points  $N_D$  and  $N_W$  which were outside the Gibbs triangle are shifted closer to the triangle along the continuation of a side of the triangle, but still remain outside the triangle. The saddle-type steady-state points  $C_F$  and  $C_W$  are now located on that side of the triangle which corresponds to the condition that the concentration of one of the constituents is zero. The junction-type steady-state point  $N_F$  remains in the interior of the triangle in both figures. Here, the trajectories which are separatrixes of the saddles  $C_F$  and  $C_W$  have physical meanings. One of the separatrixes coincides with that side of the triangle on


Fig. 6. Continuous rectification trajectories in the diagrams of zeotropic mixtures at different numbers of zero concentrations in the final products.  $a \ b \ c$  — Concentrating part of the column;  $a' \ b' \ c'$  — exhausting part of the column;  $a \ a'$  — no zero concentration;  $b \ b'$  — one zero concentration;  $c \ c'$  — two zero concentrations

which the points D (composition of the distillate) and W (composition of the bottom product) are located. The other separatrix passes in the interior of the Gibbs triangle and unites the junction  $N_F$  with the saddle  $C_F$  or  $C_W$ .

The third case, presented in Figs 6c and 6c', corresponds to the condition that two constituents have zero concentrations in the distillate or in the bottom product.

Here the junction-type steady-state points  $N_D$  and  $N_W$ , which earlier were outside the Gibbs triangle, now coincide with a vertex of the triangle, *i.e.* the external condition of the steady state is fulfilled. The saddle-type points  $C_F$  and  $C_W$  remain on the sides of the triangle corresponding to the binary mixtures of the constituents having highest and medium volatility (Fig. 6c) or medium and lowest volatility (Fig. 6c'). The junction  $N_F$ , formerly was in the interior of the Gibbs triangle, now passes to one of its sides. In this case, all trajectories within the triangles  $N_D-C_F-N_F$  and  $N_W-C_W-N_F$  have physical meanings and correspond to the various concentrations of the constituent with medium volatility in the initial mixture. It should be mentioned that the trajectories presented in Fig. 6 refer to zeotropic mixtures whose liquid-vapour diagrams do not contain a line  $\alpha_{ij} = 1$  within the Gibbs triangle. This is correct for all ideal mixtures and for the majority of zeotropic mixtures. However, there are exceptions in the latter case, which have been confirmed experimentally.

Thus far we have studied the cases corresponding to infinite heights, l, of the rectification column and to finite reflux ratios. If the process is stopped at any point of a trajectory with physical meaning, passing through the point corresponding to the composition of a final product, this is equivalent to a finite height of the column. These are the cases normally found in rectification practice. However, the investigation of the general local and non-local characteristics of the rectification trajectories within the scope of definite mass transfer models is important since it allows a better understanding of the process and serves as a scientific basis for calculations of multiconstituent rectification.

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# RECTIFICATION OF MULTICOMPONENT MIXTURES, IV

# NON-LOCAL CHARACTERISTICS OF CONTINUOUS RECTIFICATION TRAJECTORIES FOR TERNARY MIXTURES AT FINITE REFLUX RATIOS

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The non-local characteristics of rectification trajectories at finite values of the reflux ratio have been studied for non-ideal ternary mixtures containing azeotropic constituents. The main characteristics of the formation of rectification ranges with varying reflux ratios are described.

The lines of possible limiting compositions of the final products (distillate and bottom product) are determined.

It has been established that the configuration of the rectification ranges may change with varying reflux ratios. The characteristics of the degeneration and development of rectification ranges at various reflux ratios are presented.

In a previous paper [1], the local characteristics of the trajectories of continuous rectification in the vicinity of steady-state points were discussed. Also, the general characteristics of the course of trajectories in the case of zeotropic ternary mixtures were considered. It is known that the number of thermodynamically possible diagram types for ternary mixtures is 26, if antipodes and diagrams with differing deformation of the trajectories are not taken into account [2]. Each diagram type is characterized by a specific behaviour of the constituents in continuous rectification. Based on the results reported in [1], a qualitative picture of the trajectories of continuous rectification can be given for each type of diagram and the structure of the trajectory diagrams can be established. Analogous studies were carried out earlier for zeotropic mixtures whose diagrams do not contain a relative volatility line of unity,  $\alpha_{ij} = 1$ , in the interior of the Gibbs triangle, *i.e.* a line along which the distribution coefficients  $K_i$  and  $K_j$  of two constituents between the liquid and vapour phases were identical.

Let us now investigate the case of zeotropic mixtures where such a line exists. In Fig. 1 are shown the distribution coefficients in the binary mixtures constituting the ternary mixture together with the limiting values of the distribution coefficients when one of the constituent concentrations tends to zero. The line  $\alpha_{23} = 1$  passing in the interior of the Gibbs triangle is also presented.

For diagrams of the investigated type, the trajectory pattern does not differ from that considered in Ref. [1] for the cases when none of the constituents have zero concentration in the final fraction, and when one constituent has zero concentration in the final fraction. A peculiar trajectory pattern is only observed in the case when two constituents have zero concentrations in the final product, *i.e.* when  $x'_2 = x'_3 = 0$ . In this case, the equations of the trajectories indicating the composition change of the liquid phase [1] can be written in the following form:

$$\frac{dx_2}{dl} = \frac{B_2}{m} (K_2^g - m) x_2$$

$$\frac{dx_3}{dl} = \frac{B_3}{m} (K_3^g - m) x_3$$
(1)



Fig. 1. Distribution coefficient lines of constituents in binary constituents and  $\alpha_{23} = 1$  lines in ternary azeotropic mixtures. In points a and b and on the lines connecting these points,  $K_2 = K_3$  and, consequently  $\alpha_{23} = K_2/K_3 = 1$ 

where m — slope of the working line,

$$\frac{1}{B_i} = \frac{K_i^g}{\beta_i^{(x)}} + \frac{1}{\beta_i^{(y)}}$$

- $1/\beta_i^{(x)}, 1/\beta_i^{(y)}$  resistance to mass transfer in the liquid and vapour phase, respectively,
  - $K_i^g$  coefficient of equilibrium distribution of constituent i at the interface of the phases,
  - $x_i$  working concentration of constituent i,
  - l height of the column.

In points *a* and *b* (Fig. 1) the equalities  $K_2^g = K_3^g = K_a$  and  $K_2^g = K_3^g = K_b$  are valid, while  $K_q \neq K_b$ .

In an earlier paper [1] we have established that in the investigated case three lines of steady-state points exist for which  $dx_2/dl = dx_3/dl = 0$  in Eq. (1). Two of these fully coincide with the sides 1—2 and 1—3 of the Gibbs triangle, while the third line coincides with the line  $\alpha_{23} = 1$ .

Upon changing m, while maintaining the condition  $x'_2 = x'_3 = 0$ , the steady state points of the trajectories will be located on the above mentioned lines of the steady state. Let us assume that  $K_b > K_a$  and m varies within the following limits:

for binary mixture 1–2  $\lim_{x_2 \to 0} \frac{dy_1}{dx_1} < m < K_a$ for binary mixture 1–3  $\lim_{x_3 \to 0} \frac{dy_1}{dx_1} < m < K_a$ .

When m changes within these limits, the characteristic equation for the steady-state point lying on side 1—2 of the triangle (considering that  $K_2 = m$ ) will have the following form:

$$\left[ (K_3^0 - K_2) - \lambda_3 \right] \left[ x_2^{(z)} \frac{\partial K_2}{\partial x_2} - \lambda_2 \right] = 0 .$$
 (2)

Since in the composition range studied (cf. Fig. 1)  $K_3 > K_2$  and  $\partial K_2/\partial x_2 > 0$ , the roots of characteristic equation (2)  $\lambda_2$ ,  $\lambda_3$  will be positive and, consequently, the steady-state point located at side 1—2 of the triangle will be of the stable junction type.

When *m* changes within the same limits, the characteristic equation for the steady-state point lying on side 1—3 of the triangle (considering that  $K_3 = m$ ) will have the following form:

$$\left[ (K_2 - K_3^0) - \lambda_2 \right] \left[ x_3^{(z)} \frac{\partial K_3}{\partial x_3} - \lambda_3 \right] = 0.$$
(3)

In this range of compositions,  $K_3^0 > K_2$  and  $x_3^{(c)} \partial K_3 / \partial x_3 > 0$  up to point b. Consequently,  $\lambda_2 < 0$  and  $\lambda_3 > 0$ , and the steady-state point in question is of the saddle type. With increasing values of m, both steady-state points will be shifted along sides 1—2 and 1—3 of the triangle, away from its vertex 1 and will remain junction and saddle type points up to a definite moment.

Owing to the assumption that  $K_b > K_a$ , the steady-state point on side 1—2 will reach more rapidly the concentration at which  $K_2 = K_3^0 = K_a$ . When point *a* is reached,  $\lambda_3$  becomes zero and the steady-state point in question becomes a complex stable junction. At the same time, the steady-state point on side 1—3 remains a saddle.

Upon further increase of m by an infinitely small amount, the complex steady-state point breaks up into two simple steady-state points. One of these remains on side 1—2, where after having passed point a,  $K_2$  becomes greater than  $K_3^0$  (cf. Fig. 1) and, consequently, the root  $\lambda_3$  of characteristic equation (2) becomes negative, while the root  $\lambda_2$  preserves its sign. Therefore, the steady-state point on side 1—2 will be of the saddle type. The second simple steady-state point will be located on the  $\alpha_{23} = 1$  line and will be a stable junction. The characteristic equation for this point is

$$\begin{vmatrix} x_2^{(2)} & \frac{\partial K_2^g}{\partial x_2} - \lambda & x_2^{(2)} & \frac{\partial K_2^g}{\partial x_3} \\ x_3^{(2)} & \frac{\partial K_3^g}{\partial x_2} & x_3^{(2)} & \frac{\partial K_3^g}{\partial x_3} - \lambda \end{vmatrix} = 0 .$$

$$(4)$$

Upon further increase of m within the limits  $K_a < m < K_b$ , all three steady-state points will be shifted in the following directions:

1. the saddle-type point on side 1-2 will be shifted towards vertex 2 of the Gibbs triangle,

2. the saddle-type point on side 1-3 will be shifted towards vertex 3 of the Gibbs triangle,

3. the stable junction point will be shifted along the  $\alpha_{23} = 1$  line towards point b.

Upon further increase of m within the limits  $K_a \leq m \leq K_b$ , the steady-state point will finally reach point b and will merge with the saddle-type steady-state point moving alongside 1—3 to point b. At the moment when the two steady-state points merge,  $K_2^0 = K_3$  at  $x_2 = 0$  and the root  $\lambda_2$  in Eq. (3) will be zero, while the steady-state point thus formed will be a composite junction located already on side 1—3 of the Gibbs triangle.

Upon further — even infinitesimal — increase of m, this composite steady-state point becomes a simple one, but  $\lambda_2$  changes its sign and, therefore, this simple point remains a stable junction. A further increase of m up to the value of unity will bring about no further change in the trajectory pattern. It can be easily demonstrated that under the investigated conditions, the steadystate point located at vertex 1 of the Gibbs triangle will continue to be an unstable junction at all values of m. The characteristic equation for this point can be written in the form

$$[(K_2^0 - m) - \lambda_2] \cdot [(K_3^0 - m) - \lambda_3] = 0.$$
 (5)

Since  $K_2^0 < m$  and  $K_3^0 < m$  in this point, both roots  $\lambda_2$ ,  $\lambda_3$  are negative, this being the condition for the unstable junction. Thus, as opposed to the case of ideal ternary mixtures, a steady-state point of the stable junction type may appear within the Gibbs triangle in the case of zeotropic non-ideal mix-

tures with two zero-concentration constituents in the final fraction, if m has a value within a defined range.

Fig. 2 shows the sequence of changes in the structure of the trajectory diagrams at  $m \leq 1$ . Naturally, only those trajectories have physical meaning that pass through the Gibbs triangle, including sides 1—2 and 1—3 and the separatrix of the saddle-type steady-state point.

Fig. 2 indicates that in the investigated case the direction of convexity of the trajectories changes and, consequently, the presence of a concentration



Fig. 2. Development of rectification ranges in zeotropic mixtures at increasing reflux ratios for the concentrating part of the column. a-b is the line with  $\alpha_{23} = 1$ 

extremum for one or another constituent along the height of the column depends on the reflux ratio.

In the general case, liquid-vapour diagrams containing several azeotropic points are characterized by the presence of several  $\alpha_{ij} = 1$  lines passing in the interior of the Gibbs triangle. Diagrams belonging to class 1.1, type 2 are examples of such phase equilibrium diagrams [2]. Mixtures of this class and type have one binary azeotropic constituent with a minimum (or maximum) boiling temperature and one ternary azeotropic constituent of the hyperbolic type. The diagram of distillation lines is characterized in this case by three singular points of the junction type, corresponding to the vertexes of the Gibbs triangle, one singular point of the junction type, corresponding to the binary

azeotropic constituent, and one singular point of the saddle type, corresponding to the ternary azeotropic constituent.

By way of example, let us consider the generalized case of the trajectories in such a diagram under the condition that the binary azeotropic constituent has a maximum boiling temperature. The water-formic acid-acetic acid mixture yields a diagram of this type [4].



Fig. 3. a)  $\alpha_{ij} = 1$  lines for diagrams of class 1.1, type 2. b) Trajectories of rectification at infinite reflux ratio.  $N_1$  – junction-type steady-state point (binary azeotropic mixture with a maximum boiling temperature),  $C_2$  – hyperbolic azeotropic mixture. c) Lines of steady-state points of the rectification process when the distillate consists of pure constituent 1

In Fig. 3a are shown the character of the distribution coefficient lines in the binary constituents and also the  $\alpha_{ij} = 1$  lines. It can be seen that three lines,  $\alpha_{13} = 1$ ,  $\alpha_{23} = 1$  and  $\alpha_{12} = 1$ , pass through the Gibbs triangle. These lines have an intersection point,  $C_2$ , which corresponds to the hyperbolic ternary azeotropic constituent. Fig. 3b presents the trajectories of the rectification process at m = 1 and  $l = \infty$ . The trajectories form four beams, each of which corresponds to one rectification range. Let us consider the case when the constituents 2 and 3 have zero concentration in the distillate of the column operating at m < 1. Then the system of differential equations describing the trajectories can be written in the form of Eq. (1).

Fig. 3c presents the lines of the steady state along which the right sides of Eq. (1) become zero.

For binary constituent 1—3, the value of m may change within the limits  $\lim_{x_a \to 0} dy_1/dx_1 < m < 1$ . However, when m = 1, the limiting composition, *i.e.* the composition of the binary azeotropic mixture,  $N_1$ , will be reached at the bottom of the column. For binary constituent 1—2, the possible values of m

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are in the range  $\lim_{x_2 \to 0} dy_1/dx_1 < m < 1$ , the lower limit corresponding to vertex 1, the upper limit to vertex 2. Thus, similarly to the case discussed above, two lines of steady-state points exist which correspond to the variable m. In addition, a steady-state line passes through the Gibbs triangle along which  $\alpha_{23} = 1$ .

In the case under consideration,  $m = K_2 = K_3$  is the condition of the steady state. On side 1—2, the steady-state point will be shifted with varying values of  $m = K_2$  from vertex 1 to vertex 2 in the general case. This point  $C_F$  will be of the saddle type from  $x'_1 = 1$  to point a, where  $K_2 = K_3^0$ [cf. characteristic equation (2) and Figs 3a, c], since in this range  $K_3^0 < K_2$  $(\lambda_3 < 0)$  and  $x_2^{(2)} \partial K_2 / \partial x_2 > 0$ ,  $(\lambda_2 > 0)$ . In binary constituent 1—3, the second steady-state point  $N_F$  is a stable junction at all values of m, since [cf. Eq. (3) and Figs 3a, c]  $K_2^0 > K_3$ ,  $(\lambda_2 > 0)$  and  $x_3^{(2)} \partial K_3 / \partial x_3 > 0$ ,  $(\lambda_3 > 0)$ .

When the value  $m = K_2 = K_3^0$  is reached on side 1–2, the steady-state point will merge with point a and become a composite point, since  $\lambda_3 = 0$ and  $m = K_a$ . A further increase of m results in the separation of the composite point into two steady-state points. One of these, the saddle-type point  $C_F$ , begins to move along the  $\alpha_{23} = 1$  line, while the other, the stable junction  $N_F$ (since  $K_3^0 > K_2$  and  $\lambda_3 > 0$ ,  $x_2^{(2)} \partial K_2 / \partial x_2 > 0$  and  $\lambda_2 > 0$ ), continues to move along side 1–2.

All three steady-state points reach vertex 2 simultaneously, the points of the ternary and of the binary azeotropic mixtures at m = 1.

The steady-state point of the unstable junction type corresponding to the vertex 1, similarly to the preceding case, remains immobile with changing values of m. The point  $N'_D$  merges with vertex 3 at m = 1.

The changes in the structure of the trajectory diagram for various values of m are shown in Fig. 4.

This figure indicates that at  $m < K_a$ , one rectification range with a characteristic trajectory beam passing through the Gibbs triangle adjoins the vertex 1. Under the condition of  $K_a < m < 1$ , this range breaks up into two continuous rectification ranges, each being characterized by its own trajectory beam. The limiting trajectory is the one which is the separatrix of saddle  $C_F$ . The trajectories located below this separatrix, as well as those outside the Gibbs triangle, have no physical meaning.

Let us follow the movement of point  $C_F$ . Its path begins in the point where  $m = K_a$  on side 1—2. With increasing values of m, the saddle type point is shifted along the  $\alpha_{23} = 1$  line and reaches the point of the hyperbolic azeotropic constituent at m = 1.

Thus, from a definite value of m < 1, the structure of the rectification trajectories qualitatively reproduces the structure of the trajectories at m = 1, with the only difference that in a given part of the Gibbs triangle the trajectories intersect its sides, *i.e.* the closedness of the trajectories characteristic for

m = 1 is absent. The number and type of steady-state points exactly correspond to the number and type of such points in the trajectory diagram at m = 1, with the only difference that one point, *viz.*  $N'_D$ , is located outside the Gibbs triangle. The following conclusion may be drawn from these findings. At a definite value of m, the two rectification ranges in the concentrating part of the column may merge to give one range. In technological terms this means,



Fig. 4. Development of rectification ranges for diagrams of class 1.1, type 2, at varying reflux ratios, in the case when the distillate  $N_D$  consists of pure constituent 1.  $a-C_2$  is the line with  $\alpha_{23} = 1$ . The figures at the vertexes of the triangle indicate the constituents

that it is possible to bring about a transition from one range into the other by varying the reflux ratio. This method for obtaining the fraction with the desired composition will be called the method of concentration field redistribution between rectification ranges by varying the reflux ratio in given rectification columns.

The remaining cases of the rectification of mixtures of this type, *i.e.* the separation of pure constituent 3 in the distillate or of pure constituent 2 in the bottom product, can be analyzed in an analogous manner.

Let us now pass to the analysis of the trajectory diagram in the exhausting part of the column. By way of example, the mixture of class 2, type 2b [2] will be discussed. At  $l = \infty$  and m = 1, two continuous rectification ranges are found in the diagrams of this class and type. One of these ranges belongs to the tetragonal type [1].



Fig. 5. Development of rectification ranges when the bottom product consists of pure constituent 3  $(N_W)$ . The figures at the vertexe<sup>s</sup> of the triangle indicate the constituents.  $N_1$  and  $C_1$  are binary azeotropic constituents of the junction and saddle type, respectively. Diagram class 2, type 2b

In the interior of the Gibbs triangle, two  $\alpha_{ij} = 1$  lines are present. The line  $\alpha_{12} = 1$  starts from the junction point  $N_1$  which corresponds to the binary azeotropic constituent 1—2 with minimum boiling temperature and ends on side 1—3 (in Fig. 5, this line is shown by a dotted line). The line  $\alpha_{13} = 1$  starts from saddle point  $C_1$  which corresponds to the binary azeotropic constituent 1—3 with minimum boiling point and ends on side 1—2 (this line is also indicated in Fig. 5 by a dotted line). Both lines are fully located within one of the rectification ranges at  $l = \infty$  and m = 1.

Let us consider the case in which the composition of the bottom product is  $x'_3 = 1$ ,  $x'_2 = 0$ ,  $x'_1 = 0$ . By performing the analysis of the characteristic equation for the steady-state points at different values of m within the limits  $\lim_{x_1 \to 0} K_1 \ge m \ge 1$  and  $\lim_{x_2 \to 0} K_2 \ge m \ge 1$ , the series of trajectory diagrams shown in Fig. 5 is obtained.

If  $\lim_{x_1 \to 0} K_1 > \lim_{x_2 \to 0} K_2 > m > K_a$ , where  $K_a$  is the distribution coefficient of constituents 1 and 2 in point *a* lying on the  $\alpha_{12} = 1$  line, at  $x_2 = 0$ , then all rectification trajectories start from the junction point  $N_F$  located on side 1—3 of the triangle and end in point  $N_W$  where  $x_3 = 1$ . The saddle point  $C_F$ in the vicinity of which the course of the trajectories is hyperbolic lies on side 2—3. At  $m = K_a$ , the root  $\lambda_2$  of the characteristic equation becomes zero and the singular point  $N_F$ , coinciding with point *a*, becomes a composite junction. At  $m < K_a$ , this composite junction  $N_F$  separates into two simple steady-state

points. One of these is the saddle-type point  $C_F$  which, with decreasing values of m, is shifted along the side 1—3 towards the azeotropic mixture, while the other point, the junction-type point  $N_F$  moves along the  $\alpha_{12} = 1$  line towards the other azeotropic mixture located on side 1—2. Simultaneously, after passing the point in which  $m = K_a$ , the rectification range changes its configuration from the trigonal type to the tetragonal type.

At m = 1, point  $N_F$  coincides with point  $N_1$  (binary azeotropic mixture 1-2), the point  $C_F$  coincides with point  $C_0$  (pure constituent 2) and the second point  $C_F$  coincides with point  $C_1$  (binary azeotropic mixture 1-3). Simultaneously, point  $N_W$  which at all values of m, except the value of 1, is located outside the Gibbs triangle, coincides with the point  $N_0$  (pure constituent 1).

The above example clearly demonstrates the fact that the configuration of the rectification range depends on the value of m, in other words, on the value of the reflux ratio.

Similarly to the preceding cases, the size of the rectification range corresponding to the exhausting part of the column (m > 1) decreases with increasing values of m (decreasing reflux ratios).

In Fig. 6 are shown the rectification ranges for mixtures of the above class and type, under the condition that the composition of the distillate is the same as the composition of the binary azeotropic mixture 1—3 with minimum boiling temperature. At m = 0, the rectification range is a point corresponding to the distillate. With increasing values of m, two rectification ranges immediately appear. These ranges are separated from each other by the separatrix of saddle  $C'_F$ . In this case, the trajectories start from junction  $N_1(N_D)$  corresponding to binary azeotropic mixture 1—2 and end in one of the rectification range in junction  $N'_F$  located within the Gibbs triangle. In the vicinity of

saddles  $C'_F$  and  $C_F$ , the course of the trajectories is hyperbolic. With a further increase of m up to 1, both rectification ranges expand. At m = 1, the point  $N_F$  coincides with vertex 1 of the triangle, point  $C'_F$  coincides with vertex 3 and point  $C_F$  coincides with the point located on side 1—3 and corresponding to the composition of the binary azeotropic mixture. In this limiting case, the trajectories having a physical meaning occupy the total area of the triangle. The selected example is characterized by rectification ranges retaining their configuration independently of the value of m.

Thus far the boundaries of the rectification ranges were determined under the condition that the points corresponding to the composition of the distillate or of the bottom product are located on the elements of the con-



Fig. 6. Development of rectification ranges at varying reflux ratios for mixtures of class 2, type 2b in the case when the distillate consists of binary azeotropic mixture 1-3  $(N_1)$ 

centration simplex (vertexes or sides). Let us now study the case where all constituents are present in the final product of continuous rectification. In a variant of this case, the composition of the distillate is the same as the composition of the ternary azeotropic mixture with a minimum boiling temperature.

Let us study this case on the example of the diagrams corresponding to class 3.1, type 2. The mixtures belonging to one of the antipodes of the class and type in question have three binary azeotropic constituents and one ternary azeotropic constituent with a minimum boiling temperature. Let us assume that the composition of the distillate is that of the ternary azeotropic constituent. Then, at m = 0, the total rectification range degenerates into a point corresponding to the composition of the ternary azeotropic mixture. At m > 0, three rectification ranges appear, expanding with increasing values of m and occupying the total area of the Gibbs triangle at m = 1. The series of trajectory diagrams for this case is shown in Fig. 7, indicating that at m < 1, the trajectory system has seven steady-state points, repeating at a smaller scale the structure of the trajectory diagram at m = 1. In the case of m = 1, all peripheric junction-type steady-state points are located at the vertexes of the Gibbs triangle, while the saddle-type steady-state points coincide with the points corresponding to the binary azeotropic mixtures. Let us now assume that the ternary azeotropic constituent is hyperbolic and let us study the course of the trajectories on the example of diagrams belonging to class 2.1, type 3b.

We demonstrated earlier [1] that if the composition of the final product is the same as that of the ternary azeotropic constituent, the type of the steady-state point corresponding to this azeotropic mixture will not change



Fig. 7. Development of rectification ranges at varying values of m for diagrams of class 3.1, type 2. The distillate consists of the ternary azeotropic mixture  $(N_D)$  with a minimum boiling temperature



Fig. 8. Development of rectification ranges at varying values of m for diagrams of class 2.1, type 3b. The distillate consists of the ternary hyperbolic azeotropic mixture  $C_D$ 

when the value of m changes from m = 1 to any finite value. Also, the steadystate point, corresponding to the hyperbolic ternary azeotropic mixture will remain a saddle-type point in the trajectory diagram if this azeotropic mixture is the final product of the rectification. This steady-state point is reached by only two trajectories, these being the separatrixes of the saddle. Consequently, the hyperbolic azeotropic mixture can be removed as final fraction from the column only in the case when the trajectory of the process is one of the separatrixes. Naturally, to each value of m, definite separatrixes will belong, with definite slopes in the steady-state point corresponding to the hyperbolic azeotropic mixture. Fig. 8 presents the trajectories for the cases m < 1 and m = 1.

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If the final product considered is the distillate, the real trajectories at m < 1 will be the two separatrixes along which the movement is directed away from the ternary azeotropic mixture. The two other separatrixes where the direction of movement is towards the azeotropic mixture correspond to the removal of this azeotropic mixture as bottom product and have no physical meaning in the given example.

However, they do acquire a physical meaning when the composition of the ternary hyperbolic azeotropic mixture is that of the bottom product and, consequently, m > 1. In this case, all other trajectories, including the separatrixes directed away from the azeotropic point lose their physical meaning.

The discussed cases of the development of rectification ranges at varying reflux ratios for the concentrating and exhausting parts of the column, together with a detailed analysis of all thermodynamically possible diagram types, allow to formulate a number of general rules for the case when the composition of the final product corresponds to a steady-state point in the trajectory diagram.

1. In *n*-constituent mixtures at finite reflux ratios (m < 1 or m > 1), the rectification range corresponding to one trajectory beam is smaller in the general case than the rectification range corresponding to an infinite reflux ratio (m = 1).

2. The direction of convexity of the trajectories and the configuration of the rectification range remain unchanged with varying reflux ratios if the final product (distillate or bottom product) does not contain (n-1) zero-concentration constituents.

3. If the final product of the rectification contains (n-1) zero-concentration constituents and the trajectories intersect the  $\alpha_{ij} = 1$  line at  $x'_i = x'_j = 0$ , a change in the convexity of the trajectories and in the configuration of the rectification range containing these trajectories will be observed at a definite value of the reflux ratio.

4. In the case when the final product contains (n-k) zero-concentration constituents, where  $k \leq (n-1)$ , the number of rectification ranges developing from the point corresponding to the composition of the final product with varying reflux ratios is equal to the number of rectification ranges adjoining this point at infinite reflux ratio (m = 1) and infinite column length  $(l = \infty)$ .

Let us now consider a case in which the composition of the final product (distillate or bottom product) does not correspond to a steady-state point in the vapour-liquid equilibrium diagram.

Earlier we demonstrated [1] that for the studied model characterized by ideal countercurrent and by the distribution of resistance to mass transfer between both phases, at finite reflux ratios (m < 1 or m > 1) the trajectories of the rectification for the liquid and vapour phases are tangential to the

liquid-vapour node that characterizes the equilibrium between the interface concentrations  $x_i^g$  and  $y_i^g$  in the point  $x_i'$  corresponding to the final product.

The point  $x'_i$  divides this node into segments inversely proportional to the phase resistances  $1/\beta_i^{(x)}$  and  $1/\beta_i^{(y)}$ .

In the case of infinite reflux ratio (m = 1), the nodes of this type are tangential to the trajectories in any point which will also divide the node into segments inversely proportional to the phase resistances. Thus, the condition realized in the point of the end product at  $m \neq 1$  will be fulfilled in all points of the trajectories at m = 1. At a fixed composition of the end product, changes in m result in the formation of a trajectory beam composed of trajectories all of which will be tangential to the node  $\overline{\chi_{gyg}^g}$  and will be located on one side of this node. However, in view of the fact that the curvature of the trajectories increases with the extent of m deviating from 1, all trajectories at  $m \ll 1$  will be located on one side of the trajectory corresponding to infinite reflux ratio (m = 1). This is illustrated in Figs 9a and 9b. Thus the trajectory of the process at m = 1 is a limiting trajectory in the sense that all other trajectories for which  $m \neq 1$  are located at one side of the limiting trajectory. Naturally all characteristics discussed above apply to the vicinity of the point corresponding to the final product of the rectification, under the condition that this point is not a steady-state point. Actually in this case all trajectories of the rectification process at  $m \neq 1$  are tangential to the limiting trajectory on that side towards which the latter is concave (cf. Figs 9a and 9b).

The set of limiting trajectories yields the trajectory diagram at m = 1and  $l = \infty$  [1].

Each trajectory diagram of this type contains ordinary trajectories and trajectories that are separatrixes of saddles. The latter divide the total space of the simplex (e.g. the Gibbs diagram) into separate rectification ranges corresponding to the condition m = 1 and  $l = \infty$ . The ordinary trajectories form characteristic beams. Their pattern in the concentration simplex determines the configuration of the rectification ranges. Each beam corresponds to one rectification range. Their analysis indicates that if the composition of the distillate or of the bottom product lies on an ordinary limiting trajectory, then, independently of the value of m, the trajectory having a physical meaning, will lie in that rectification range to which the above ordinary limiting trajectory corresponds.

The most interesting case is the one where the composition of the final product at  $m \neq 1$  lies on the limiting trajectory which separates two rectification ranges from each other at m = 1 and  $l = \infty$ .

In this case, the trajectories of rectification at  $m \neq 1$  break up into two beams. Each of these beams lies in one of the rectification ranges and is tangential to the limiting trajectory in the point corresponding to the composition of the final product (distillate or bottom product).

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These characteristics are presented in Figs 9c and 9d for the distillate and the bottom product, respectively.

Thus, within the scope of the investigated mass transfer model, in the general case the composition lying on the separation line of the rectification at m = 1 and  $l = \infty$  will be the possible limiting concentration of the final product.



Fig. 9. Cases of the limiting composition of the end products. a and c — distillate, b and d — bottom product. a and b — the composition of the end product lies on the ordinary trajectory corresponding to the condition of m = 1. c and d — the composition of the final product lies on the separation line of rectification corresponding to the condition of m = 1

If the resistance to mass transfer is concentrated in the vapour phase, the line of the possible limiting compositions of the end product will be the separation line of distillation, *i.e.* the line which divides the concentration triangle into ranges of free equilibrium evaporation.

If the resistance to mass transfer is concentrated in the liquid phase, the line of the possible limiting compositions of the end products will be the separation line of condensation, *i.e.* the line which divides the concentration triangle into ranges of free equilibrium condensation.

In this paper the rectification ranges corresponding to so-called incomplete columns, *i.e.* columns consisting of one concentration or exhausting part, were discussed. For complete columns, the presence of two trajectory beams is characteristic, one of these corresponding to the concentrating part of the column (m < 1), the other to the exhausting part (m > 1). The trajectories of these beams are correlated pairwise by the overall material balance equation for each constituent and by the material balance equation for the material flows at the feed level of the column. However, in view of the characteristics described above, it is fully evident that the trajectories having physical meaning will be located in one rectification range, viz. in that range where the composition of the initial mixture being rectified is contained [2].

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# INVESTIGATION OF ADSORPTION PHENOMENA ON PLATINIZED Pt ELECTRODES BY TRACER METHODS, XII

## STUDIES ON THE ADSORPTION OF n-PROPANOL

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The adsorption of n-propanol on a platinized Pt electrode has been investigated by tracer methods. The process has proved to be an irreversible chemisorption that cannot be characterized by an equilibrium isotherm. The apparent concentration and potential dependences of adsorption are presumably due to certain oxidation-reduction reactions.

In connection with our investigations on the oxidation of *n*-propanol on a platinized platinum electrode a number of questions has arisen concerning the adsorption of the alcohol. The most important problems were connected with the reversibility of adsorption, the existence of adsorption equilibrium, and with the form of the adsorption isotherm. For solving these problems, the mobility of the adsorbed molecule and the potential and concentration dependences of the adsorption were to be studied.

Based on our previous investigations concerning first of all *i*-propanol [1], it has been assumed that the application of tracer methods will be helpful also in this case for elucidating the relation between adsorption and oxidation.

## Experimental

Measurements were carried out in 1N HClO<sub>4</sub> solution by a method already described [2]. For the experiments <sup>14</sup>C-labelled *n*-propanol of 0.1 to 10 mCi/mol specific activity was used. The electrode potential values given in this paper are referred to a 1 atm hydrogen electrode immersed into 1N HClO<sub>4</sub>.

## Results

As far as the concentration dependence of adsorption is concerned it has been found that starting from very low concentrations, at certain potential values, the adsorption within the experimental error (10%) is independent of the concentration (see Fig. 1).

The behaviour of the adsorption as a function of potential was observed to depend first of all on the potential at which the measurement was started, and on the direction of potential change during the experiment. The count rate vs. potential curve in Fig. 2 was obtained by starting the measurement at 0 mV and proceeding in the direction of positive potentials. When starting the measurement at 400 mV and changing the potential toward 0 mV, an enormously high amount of substance remains on the electrode even at 0 mV (see Fig. 3, curve a). The substance remaining on the electrode can be removed only by strong anodic polarization. On the other hand, when starting the measure-



Fig. 1. Variation of the count rate at 400 mV with time. Concentration: 1:  $6 \times 10^{-5}$  mol/1; 2:  $3 \times 10^{-4}$  mol/1



Fig. 2. Potential dependence of adsorption at an n-propanol concentration of  $3 \times 10^{-4}$  mol/1. Starting potential: 0 mV

ment at 0 mV after an anodic regeneration, sometimes higher absorption was observed at 400—500 mV than at the beginning (see Fig. 3, curve b). (The count rate proportional to the amount of adsorbed substance generally depends very much on the pre-treatment of the electrode, *i.e.* on the extent of the removal of very strongly adsorbed impurities.)

When starting the measurement at very positive potentials (higher than 400-500 mV), and increasing the potential during the experiment, the curves depending on the concentration become slightly different, as it can be seen in Fig. 4.





Fig. 3. The hysteresis of adsorption Fig. 4.

Fig. 4. Potential dependence of adsorption at a concentration of  $10^{-4}$  mol/1. Starting potential: 500 mV



Fig. 5. Polarization curve at 0.3 mol/1 propanol concentration. Galvanostatic method

The experimental facts given above appear to be rather contradictory and not easily interpretable. In the interpretation of the experiments, of course, the oxidation of the alcohol at potentials above 500 mV should also be taken into account. This latter requirement is demonstrated by the polarization portion of the galvanostatic curve (Fig. 5), obtained for propanol at a concentration (0.3 mol/l) much higher than the range studied here. The main problem is to find the steady-state or equilibrium processes that play a role in the observed adsorption phenomena. The problem can be solved by studying the mobility of adsorbed molecules.

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Fig. 6. Desorption in the pure background solution



Fig. 7. Desorption in the presence of unlabelled n-propanol

For this purpose, the desorption rate and the exchange between the adsorbed and solution phases were investigated in our previous work. Labelled n-propanol was adsorbed on the electrode (at 300 mV), then, after the removal of the solution containing the labelled substance, the cell compartment holding the electrode was refilled either with pure background solution (Fig. 6), or with a solution containing unlabelled n-propanol (Fig. 7). The behaviour of the adsorbed molecules can be investigated conveniently by this method. In Figs 6 and 7 an arrow indicates the time at which the solution was changed or unlabelled propanol was added.

It can be concluded from the curves that the molecules adsorbed at 300 mV do not leave, or leave only extremely slowly the surface at the same potential. The situation remains essentially the same at 400 and 200 mV. At more negative potentials the amount of the adsorbed labelled substance decreases, a considerable part of it, however, still remains on the surface without taking part in the reaction or in the exchange. This permanently bonded fraction can be removed by oxidation only at 500 mV or at even higher potentials.



Fig. 8. Preadsorption with n-propanol, washing, then addition of labelled propanol in  $1.5 \times 10^{-4}$  mol/1 concentration (at 300 mV)

The conditions of adsorption can be studied even better in experiments where labelled propanol is present in the solution and the preadsorption is carried out with the unlabelled compound. Fig. 8 refers to an experiment of this type. As the surface is covered with strongly bonded unlabelled compound, no increase of the count rate is observed at 300 and 400 mV. At 500 mV the adsorption of the labelled compound increases. It was shown in Fig. 6 that part of the adsorbed substance is removed from the surface at 500 mV. This latter experiment, on the other hand, shows that adsorption on the surface occurs in this case too. When the potential is changed to 600 mV, the count rate increases for a while, the same being observed at 800 mV. At higher potentials, however, only desorption can be observed.

Before proceeding to the interpretation of the experimental facts, it is necessary to describe the investigations concerning the adsorption of the oxidation products of *n*-propanol.

In the oxidation process of the alcohol, as was shown by our experiments not discussed here, first propionaldehyde, then propionic acid is formed [3].

Taking into account that in the tracer experiments rather low alcohol concentrations are employed, the total amount of alcohol can be oxidized in a relatively short time at 800—1000 mV. This is proved, first of all, by the fact that the character of the potential dependence of the adsorption changes, as is shown in Fig. 9. In this range the shape of the count rate vs. potential curve



Fig. 9. Potential dependence of the adsorption of oxidation products (starting concentration:  $10^{-4}$  mol/1)



Fig. 10. Variation of the count rate upon changing the initial specific activity  $(a_0)$  by adding propionic acid

becomes independent of the direction of potential change. The shape of the curve in Fig. 9 is essentially the same as that found for the adsorption of acetic acid [4]. In order to prove that the adsorption phenomenon is indeed the adsorption of propionic acid, the changes caused by the dilution with unlabelled propionic acid at a given potential have been studied. Provided that the in-

crease of concentration does not significantly increase the adsorption, it is very probable that the labelled substance has been really converted to propionic acid, if the addition of propionic acid reduces the observed count rate proportionally.

Count rates measured at 600 mV, after the specific activity  $(a_0)$  has decreased to 1/2 and 1/4 of its original value, are given in Fig. 10. Combining the facts given above and the information in Fig. 10, it appears doubtless that the curve given in Fig. 9 represents the potential dependence of the adsorption of propionic acid. It is to be noted that at the adsorption maximum of the product (at about 800 mV) the count rate is much higher (29,000 cpm, see Fig. 2; specific activities are the same in both cases). This fact leads to the conclusion that, provided that in the case of alcohol the surface is completely covered, the steric requirement of propionic acid molecules is much lower than that of propanol, and that the two types of molecules are arranged on the surface in a different manner. This is also supported by the fact that the mobility of the adsorbed propionic acid is substantially higher than that of the alcohol. The adsorbed, labelled propionic acid can easily be exchanged for inactive propionic acid.

# Interpretation of experimental results and conclusions

On the basis of the experimental results one might first conclude that, even if the disturbing effect of the oxidation reaction is disregarded, an adsorption equilibrium for the alcohol, at least on a considerable part of the surface, cannot be assumed. The adsorption taking place at 300—400 mV is an irreversible chemisorption process, during which, presumably, dehydrogenation processes take place. A considerable part of the adsorbed molecules formed in this process, however, is so strongly bonded to the surface that it cannot be removed from the surface by hydrogenation, not even at 0 mV. At the same time, the fact that in the experiments starting at 0 mV (Figs 2 and 3) the extent of adsorption is still low at 100—200 mV, also indicates that dehydrogenation may play a role in the adsorption process, and that the adsorption process begins only if the potential is changed in the positive direction, *i.e.* in the direction of decreasing hydrogen coverage.

It can be seen from the foregoing that the oxidation reaction is not preceded by an adsorption equilibrium, *i.e.* there are only irreversible steps (transport phenomena, adsorption, reaction) in the process converting alcohol to aldehyde or acid. Each of these elementary processes may depend on the concentration and/or potential, but the relation between the adsorbed amount and the potential in the overall process cannot be attributed to a single step, *e.g.* adsorption. This should be emphasized since the experimental adsorbed amount vs. potential, or adsorbed amount vs. concentration plots are regarded, in several cases, as the potential dependence of the adsorption or an adsorption isotherm.

The question of whether the adsorbed molecules actually take part in the oxidation reaction yielding aldehyde or acid, respectively, deserves particular attention. It is certain that at least a part of the molecules does not, since otherwise in the presence of inactive propanol the labelled propanol previously adsorbed on the surface should be completely removed from the surface at a relatively low potential value (400—500 mV), owing to the oxidation.

It has been assumed that the aldehyde molecules may be strongly adsorbed on the surface of the electrode. Indeed, in the presence of propionaldehyde no adsorption of propanol has been observed. At the same time, investigations of different nature have shown that even in the presence of propionaldehyde the oxidation of alcohol takes place at an appreciable rate [3]. Generally, below 800 mV platinum electrodes, the rate of the oxidation of alcohols is higher than that of aldehydes at the same potential [5, 6]. (This is why aldehydes can be prepared from alcohols on a platinum electrode.) Based on the above facts it seems likely that the aldehyde formed from alcohol is enriched on the surface and the apparent potential dependence of the adsorption of alcohol, beyond 400 mV, is determined by the oxidation process of the adsorbed aldehyde. Consequently, the oxidation of alcohol to aldehyde can also take place on a surface that is practically completely covered with aldehyde. This fact is not surprising at all; a similar phenomenon has been observed in the oxidation of i-propanol [1]. In this case it could be proved that the adsorbed molecules do not take part in the reaction.

On the basis of the above discussion we think it is understandable why do the obtained results vary, both when studying the oxidation reaction and when investigating the adsorption phenomenon, with the conditions of experiments, *e.g.* with the initial value of the potential and with the direction of potential change.

Further complications may arise due to the fact that in adsorption studies using tracer methods, in the low alcohol concentration range, the adsorption of the end-product (*i.e.* propionic acid) might also play a role. Since the adsorption of propionic acid is a reversible process, whereas that of *n*-propanol is irreversible, *i.e.* the latter is much more strongly adsorbed, the disturbing effect due to the adsorption of propionic acid has no importance until the concentration of the alcohol in the immediate vicinity of the electrode surface is not substantially lower than that of the acid.

The exact interpretation of the phenomena meets with difficulties. The main goal of this work was, first of all, to collect information that will serve as a basis for the study of the kinetics and reaction mechanism of the oxidation of *n*-propanol.

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# SPECTROPHOTOMETRIC OBSERVATIONS ON THE REACTIONS OF 2,3-DICHLORO-5,6-DICYANO-*p*-BENZOQUINONE WITH VARIOUS DONORS

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Spectrophotometric studies in chloroform of the reaction between 2,3-dichloro-5,6-dicyano-*p*-benzoquinone with acenaphthene, diphenylamine, *o*-toluidine are reported. The results indicate that in all cases charge-transfer bands appear initially which vanish with the simultaneous emergence of a band near 340 nm. The nature and the origin of this band are discussed.

Charge transfer complexes are known to be formed as the first step in many reactions involving 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). As yet, however, little is known about the stability of these complexes. The durene-DDQ complex is reported to be unstable [1], however, the naphthalene-DDQ complex in methylene chloride is stable for at least 48 hours [2]. FOSTER and HORMAN have observed that several aromatic hydrocarbons forming charge transfer complexes with DDQ undergo subsequent irreversible reaction [3]. The importance of DDQ and its reactions has been emphasised recently [4]. In a previous work done in this laboratory with the system DDQ and benzene [5], a charge-transfer band at 427 nm was found, which decreased in intensity with time and by the simultaneous emergence of a new band near 355 nm. It has been of interest to perform a further systematic study on spectral changes during the interaction in order to understand the complete reaction sequence.

## Experimental

Pure 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) was obtained from Light & Co. It was further purified by crystallizing from chloroform. Acenaphthene and diphenylamine were purified by repeated crystallizations from absolute ethanol, while o-toluidine was distilled under reduced pressure just before use. Analar chloroform obtained from B.D.H. was used as a solvent for the present studies without further purification.

Spectrophotometric studies were carried out on a Unicam SP-500 spectrophotometer using 10 mm matched silica cells. The measurements were made at room temperature (30 °C  $\pm$   $\pm$  2.0 °C). Since the absorption due to DDQ was appreciable in the wavelength region under study, its concentration was kept much below the donor concentration. The absorption due to the presence of DDQ was eliminated by using a reference solution with the same DDQ concentration.

## **Results and discussion**

When the colourless solutions of different donors are mixed with the yellow solution of DDQ, a distinct change in the colour occurs. The resultant initial colour, however, fades with time and is replaced by another colour. The following table gives the informations on the visual observations.

# Table I

Colour mixtures of DDQ with different donors in chloroform

Colour just after mixing	Colour after a certain period of time		
yellow	intense yellow		
green	red		
violet-blue	pink-red		
green	pink-red		
	Colour just after mixing yellow green violet-blue green		

The colour changes have been found to be faster when higher donor and acceptor concentrations were used.

In the four systems with DDQ as acceptor and benzene, acenaphthene, o-toluidine and diphenylamine as donors, the spectrophotometric studies show the presence of new bands in the region 400—700 nm which are attributed to CT transitions. (Benzene at 427 nm, acenaphthene at 490 and 720 nm, o-toluidine at 690 nm, and diphenylamine at 700 nm.) However, the intensity of these CT bands diminishes in time and a new band is seen to gain in intensity near 340 nm (Figs 1—3). If the initial band is supposed to be a CT transition band, the decrease in its intensity in time is due to a decrease in the concentration of the charge-transfer complex.

In the initial stage the complex has the characteristics of a CT complex, *i.e.* the ground state of the complex is an admixture of the ionic state  $(D^+ A^-)$ and the no bond state (DA), the contribution of the latter being predominant. On standing, however, a complete transfer of an electron from the donor to the acceptor occurs, and an ion pair is formed:

 $D + A \rightleftharpoons D, A \rightleftharpoons D^+A^-$ 

Such a mechanism has been previously proposed by MULLIKEN and REID [6] for the pyridine-iodine complex. The intensity increase of the band at 340 nm is not due to a CT complex but to the emergence of an ion pair (inner complex).

The band at 340 nm cannot be attributed to the donor, as it has no absorption bands in this region. Benzene, although having its forbidden singlettriplet transition band in this region, cannot possibly gain that much in intensity [7].

It is of interest to note that although acenaphthene shows a more pronounced interaction than naphthalene, the shape of the band and its position

are independent of the nature of the donors. Also, a shoulder appearing around 370 nm in the solution spectra of pure DDQ is observed to be absent in DDQaromatic hydrocarbon, but present in DDQ-amine systems.

Solid state spectra of *p*-benzoquinone and related compounds have been studied by SIDMAN [8], and of DDQ in solution by BURSTEIN and RINGOLD [9].



The  $L_b$  band polarized along an axis perpendicular to the line joining the oxygen atoms of quinone is the weaker  $\pi \to \pi^*$  transition occurring at 340 nm. The  $n \to \pi^*$  transition in the weak absorption region is expected at higher wavelengths [10].

The intensification of the band at 340 nm in solution can be explained on the basis of the reaction mechanism proposed by FOSTER and HORMAN [3].

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Fig. 2

In the system DDQ-polyaromatics the final reaction product isolated from the mixture was the following:



where (D-) is a donor molecule short in one of its protons.

In the above sigma complex configuration the quinone chromofore has been transformed into a benzene chromofore. Such substituted benzenes [11] are known to absorb near 340 nm. The spectral changes in DDQ-hydrocarbons

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Fig. 3

have to be explained, therefore, in terms of the rate and amount of such chromofore changes. The  $L_a$  band may also become allowed and contribute to the increased intensity. These spectra do not show  $n \to \pi^*$  transitions which further support the view that quinone chromofore is not maintained in such interactions.

The above mechanism explains well the intensification of band at 340 nm when DDQ reacts with hydrocarbons. When amines react with DDQ,

besides intensification of the 340 nm band, a shoulder near 370 nm is also observed. This suggests that quinone chromofore is probably not disturbed by the reaction of DDQ with amines. NAGAKURA [12] has suggested the following formula which maintains the quinone chromofore:



In such cases the intensification has to be explained on the basis of interaction between the transition moments of the donor and acceptor molecules. Charge resonance could also contribute to a rise in intensity. A theoretical analysis of the various factors responsible for intensification might be of interest.

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# INFRARED SPECTRA OF Ni(II) PYRIDINE, PICOLINE AND LUTIDINE COMPLEXES

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The infrared spectra of Ni(py)<sub>2</sub>X<sub>2</sub>, Ni(py)<sub>4</sub>X<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>) and Ni(4-Y-py)<sub>4</sub>Cl<sub>2</sub> (Y=methyl, ethyl, propyl, vinyl; 3-methyl) complexes are interpreted in the 375–8750 cm<sup>-1</sup> region. The in-plane and out-of-plane ring-deformation vibrations of the aromatic ligand appearing at about 610 cm<sup>-1</sup> and 410 cm<sup>-1</sup>, as well as the v(Ni—N) and v(Ni—X) vibrations in the low-energy region are suitable for the determination of the geometry of the structure.

It is well known that the substituents of ligands significantly affect or determine the composition, structure, bonding conditions, etc., of a complex molecule. Pyridine and its methyl derivatives (further on, pyridine, picoline and lutidine will be denoted as py, pic, and lu, respectively) form stable compounds of well-defined composition with the nickel(II) ion. The compositions and structures of these molecules, depending on the nature of the substituent and the anion, are the following: (a) Ni(base)<sub>2</sub>X<sub>2</sub> (square planar, tetrahedral or polymer octahedral; Structures I—III); (b) Ni(base)<sub>4</sub>X<sub>2</sub> (distorted octahedral; Structure IV) (Fig. 1). Moreover, Ni(py)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub> and Ni(py)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub> molecules have also been isolated or detected.

In the present paper infrared spectra in the region  $375-8750 \text{ cm}^{-1}$  of  $\text{Ni}(\text{py})_2 X_2$ ,  $\text{Ni}(\text{py})_4 X_2$  (X = Cl<sup>-</sup>, Br<sup>-</sup>) and  $\text{Ni}(\text{base})_4 \text{Cl}_2$  (base = 4-pic, 4-ethylpy, 4-propyl-py, 4-vinyl-py) complexes are discussed.

# Experimental

The compounds were prepared by mixing absolute ethanolic solutions of NiX<sub>2</sub> with the ligand in the mole ratios 1:2.1 and 1:4.2, respectively [1-4]. After prolonged cooling the product was filtered off, washed with ethanol containing 5% of the base, and dried over  $P_2O_5$ . The composition of the product was checked by C, H and Ni analysis.

The infrared spectra were recorded with a Unicam SP 100 spectrophotometer in KBr pellets. 2 mg of the complex was comprised in pellets of 400 mg weight.

## **Results and discussion**

The infrared spectra of the compounds listed above are discussed in two groups — partly on the basis of literature data. First the characteristic frequencies of the coordinated ligands are dealt with; in the second part the Ni-base and Ni-X valence vibrations are treated. The former vibrations are usually shifted in the complexes towards higher energies and the extent of this shift depends on the stereochemical conditions prevailing in the molecule and on the central ion, while it is practically independent of X. The Ni-X vibrations are mostly characterized by the  $\nu(Ni-N) < \nu(Ni-X)$  relationship.



The bands appearing in the infrared spectrum of the pyridine molecule of  $C_{2\nu}$  symmetry in the range 375—1800 cm<sup>-1</sup> are given in Table I. The frequency values are in good agreement with the data of other authors. The notation of frequencies corresponds to that used by KLINE and TURKEVICH [5].

The ring vibrations, treated in the first approximation analogously to the normal vibrations of benzene [6], can, in general, be identified definitely in the infrared spectrum; this does not hold for the hydrogen vibrations, and the opinions of different authors are not undivided in their assignments [7-9].

In the complex, the bands of the free base are shifted towards higher frequencies. It can be stated, however, that only few alterations show systematic relationship with the electronegativity, mass, etc., of the metal. It was found [10] that in several MeL<sub>2</sub>X<sub>2</sub> compounds the positions of the 6*a* ( $a_1$ , inplane ring deformation) and 16*a* ( $b_2$ , out-of-plane ring deformation) vibrations at about 620—630 cm<sup>-1</sup> and 410—440 cm<sup>-1</sup> show a regular change (Table II). It is also known that the energy of the 6*a* vibration is more sensitive to stereochemical changes (Table III) [10].
## Table I

				-		
Pyridine	Ni(py)2Cl2	Ni(py),Cl2	Ni(py)2Br2	Ni(py)4Br2	Type of	vibration
1582	1614 s	1613 s	1614 s	1612 s	8a	(A <sub>1</sub> )
	1608 s	1608 s	1609 s	1607 s		
1572	1581 w	1582 w	1583 w	1581 w	86	(B <sub>1</sub> )
1485	1498 m	1498 m	1498 m	1496 m	19a	(A <sub>1</sub> )
1437	1455 s	1455 s	1456 s	1453 s	196	(A <sub>1</sub> )
_	1397 w	1394 w	1393 w	1391 w		
_	1374 w	1374 w	1372 w	1369 w	14	$(B)_2$ ?
1215	1232 m	1231 m	1232 m	1230 m	3	(B <sub>1</sub> )
1144	1164 w	1163 w	1164 w	1161 w	9a	(A <sub>1</sub> )
1067	1082 m	1082 m	1082 m	1082 m	17a	(A <sub>2</sub> )
1028	1054 m	1054 m	1054 m	1051 m	12	(A <sub>1</sub> )
~1007	1024 m	1026 m	1024 m	1022 m		
$\sim 993-$	1009 w	1010 w	1009 w	1008 w		
938	987 w	984 w	985 w	983 w	1	(A <sub>1</sub> )
	957 w	956 w	?	955 w	1.00	
-	764 m	762 m	764 m	762 m	10a	$(A_2)$
708	701 m	701 m	701 s	701 s	1	
605	636 m	629 m	637 m	630 m	6a + 6b	$(A_1 + B_1)$
	532 m	530 m	530 m	530 m		
404	437 w	430 w	439 w	430 w	16a	$(A_2)$

Infrared spectral data of  $Ni(py)_n X_2$  compounds\* (n = 2, 4; X = Cl<sup>-</sup>, Br<sup>-</sup>)

\* s: strong, m: medium, w: weak.

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Table II

The change of 6a and 16a vibrations by different transition metal complexes

6a	16a
627	419
629	424
631	429
634	439
644	441
	6a 627 629 631 634 644

#### CSÁSZÁR: INFRARED SPECTRA OF COMPLEXES

#### **Table III**

The wavenumbers of 6a an	nd 160	<i>vibrations</i>	by	some	Co(II)
complexes with differe	nt ster	eochemical	arre	angem	ent

Complex	6a	16a
Co(py) <sub>2</sub> Cl <sub>2</sub> (quasi-tetrahedral)	642	422
Co(py)2Cl2 (polymeric octahedral)	631	422
Co(py) <sub>4</sub> Cl <sub>2</sub> (quasi-octahedral)	625	422

The great similarity of the spectra of free and coordinated pyridine indicates an almost unchanged electron density of the ring, which may be attributed to back-coordination, among other factors [11]. Although no unequivocal evidence exists for back-coordination in the pyridine complexes, this hypothesis is useful from the point of interpretation of the experimental data. The spectral data of four pyridine complexes are listed in Table I and two characteristic examples are shown in Figs 2 and 3.



Fig. 2. Infrared spectrum of Ni(py)<sub>4</sub>Cl<sub>2</sub> in the region 375-1800 cm<sup>-1</sup>

Concerning the spectra of pyridine derivatives reference can be made to the literature [12—15]. It should be noted that these spectra are much more complicated than that of the parent compound, therefore the identification of the bands is a greater problem. The spectral data of some 4-alkyl-pyridine complexes are given in Table IV; the spectrum of Ni(4-ethylpyridine)<sub>4</sub>Cl<sub>2</sub> is shown in Fig. 4.



Fig. 3. Infrared spectrum of Ni(py)<sub>4</sub>Br<sub>2</sub> in the region 375-1800 cm<sup>-1</sup>

It is seen that in the spectra of 4-ethylpyridine and 4-propylpyridine complexes a single sharp band appears at 1233 cm<sup>-1</sup> and 1232 cm<sup>-1</sup>, respectively, while in the case of the methyl and vinyl derivatives these bands are split (1239 + 1211 cm<sup>-1</sup> and 1233 + 1216 cm<sup>-1</sup>). The out-of-plane ring deformational vibration band found between 820 cm<sup>-1</sup> and 850 cm<sup>-1</sup> appears at 820, 839, 848, 836, 810, 848 cm<sup>-1</sup> in the methyl, ethyl, propyl and vinyl derivatives, respectively. The bands absorbing between 1600 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> can be assigned to the C=C and C=N vibrations of the pyridine ring.

From the aspect of bonding conditions and structure, the region below 400 cm<sup>-1</sup> comprising the  $\nu(\text{Ni}-\text{N})$  and  $\nu(\text{Ni}-\text{X})$  vibration bands is the most interesting. The types and number of the infrared active vibrations possible in various geometries can be found in Table V [10].

The v(Ni-N) values of some complexes are given in Table VI [16-18].

In distorted tetrahedral molecules, two  $\nu(Ni-X)$  and  $\nu(Ni-N)$  vibrations each are possible. According to the data available, the  $\nu(Ni-X)$  bands can be detected in the Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> compounds, and so can one of the  $\nu(Ni-N)$  bands; the other falls probably below 200 cm<sup>-1</sup>. In molecules of iden-



Fig. 4. Infrared spectrum of Ni(4-ethylpyridine)<sub>4</sub>Cl<sub>2</sub> in the region  $375 - 1800 \text{ cm}^{-1}$ 

tical type, the v(Ni-N) vibrations appear practically at identical frequencies. In the case of identical base and varying X, the changes are slight in the v(Ni-N) bands, while they are considerable in the v(Ni-X) bands. In tetrahedral molecules, the ratios  $v_{\text{Br}}/v_{\text{Cl}} \sim 0.77$  and  $v_{\text{I}}/v_{\text{Cl}} \sim 0.65$  have been observed [10, 19-21]. The v(Ni-X) frequencies for tetrahedral NiX<sub>4</sub> molecules are always lower than those for the distorted tetrahedral NiL<sub>2</sub>X<sub>2</sub> compounds (Table VII) [10, 22].

In the vibration spectrum of a  $NiL_4X_2$  distorted octahedral compound  $(D_{4h})$  one valence vibration band is expected. The energies of the  $\nu(Ni-N)$  vibrations are very close to one another.

#### CSÁSZÁR: INFRARED SPECTRA OF COMPLEXES

rarea s	spectrat aata o	j compounds o	<i>f</i> the 11( <b>1</b> -1- <i>j</i>	$p_{j}_{4}$ $\sigma_{2}$ $r_{j}$ $p_{e}$
=	Methyl	Ethyl	Propyl	Vinyl
	1623 s	1622 s	1620 s	1619 s
	1566 w	1562 w	1560 w	1554 m
	1511 m	1507 m	1506 m	1509 m
	1445 m	1467 m	1470 m	-
	1431 m	1433 s	1433 s	1425 s
	1392 w	1389 w	1389 w	
	1239 m	1233 m	1232 s	1233 s
	1221 m	-	_	1216 w
	1116 w	1120 w	_	1116 w
	1079 w	1076 m	1074 m	1077 m
	1028 m	1026 m	1026 m	1021 m
	990 w	983 w	988 w	1000 m
	<u> </u>	_	_	940 m
		_	880 w	880 w
	820 s	839 s	836 m	848 s
	_	-	810 s	807 m
	_	788 w	-	-
	731 m	- · · ·	759 w	740 m
	710 w	720 w	_	
	_	_	_	649 w
		_	607 m	-
	549 w	508 m	589 w	575 m
	503 m	509 m	516 m	-
	_	_		477 m
				-

 Table IV

 Infrared spectral data of compounds of the Ni(4-Y-py), Cl. type

Y

In polymeric octahedral  $(C_i)$  molecules there are two short and two long metal-halogen bonds; two v(Ni-X) and one v(Ni-N) vibrations are infrared active. Three bands can be recorded between 200 cm<sup>-1</sup> and 400 cm<sup>-1</sup>; two of them show a ratio of  $v_{\text{Br}}/v_{\text{Cl}} \sim 0.86$ , thus they can be supposed to be v(Ni-X) bands. The third band, independent of X, belongs to the v(Ni-N) vibration. It should be noted that the structures of the spectra of polymeric octahedral molecules are never so well defined as those of the corresponding monomeric molecules.

Although none of the examples given in this paper represents this type of compounds, it should be mentioned that one band is expected for a distorted planar compound; the energy of the  $\nu(\text{Ni}-X)$  vibrations is the greatest in this case [10].

## Table V

The number and the type of the infrared active Ni-X and Ni-N vibrations by nickel(II) complexes with different symmetry

	Geometry	v(Ni—X)	Infrared active	ν(Ni—N)	Infrared active
$NiL_2X_2$	quasitetrahedral ( $C_{2v}$ )	$a_1 + b_1$	2	$a_1 + b_2$	2
	distorted planar $(D_{2h})$	$a_g + b_{3u}$	1	$a_g + b_{2u}$	1
	polymeric octahedral ( $C_i$ )	$2a_g + 2a_u$	2	$a_g + a_u$	1
$\rm NiL_4X_2$	distorted octahedral $(D_{4h})$	$a_{1g} + a_{2u}$	1	$a_{1g} + b_{1g} + e_u$	1

#### **Table VI**

Complex	Geometry	v(Ni—N)
Ni(py) <sub>2</sub> Cl <sub>2</sub>	pO	244
$\mathbf{Br}_{2}$	pO	245
$(NSC)_2$	pO	230
$I_2$	kT	240
Ni(2-pic) <sub>2</sub> Cl <sub>2</sub>	kT	239
$Br_2$	kT	239
Ni(py) <sub>4</sub> Cl <sub>2</sub>	kO	242 + 236
Br <sub>2</sub>	kO	235
$I_2$	kO	240 + 228
$(NCS)_2$	kO	232
$Ni(3-pic)_4(NCS)_2$	kO	240

v(Ni-N)	frequencie	es of some	complexes
of the	$NiL_2X_2$ a	nd NiL <sub>4</sub> X <sub>5</sub>	type

#### **Table VII**

Ni-X stretching vibrations of tetrahedral and distorted tetrahedral nickel(II)complexes

Complex	Vibration	cm <sup>-1</sup>
(NiCl <sub>4</sub> ) <sup>2</sup> -	v(Ni-Cl)	285
Ni(2-pic) <sub>2</sub> Cl <sub>2</sub>		327 + 297
$(NiBr_4)^2 -$	v(Ni-Br)	224
Ni(2-pic) <sub>2</sub> Br <sub>2</sub>		256
$(NiI_4)^{2-}$	v(Ni-I)	189
Ni(2-pic) <sub>2</sub> I <sub>2</sub>		230

According to the above facts, the positions of the  $\nu(Ni-X)$  bands can also be very different in the various geometrical forms. In general, the order is: planar > quasitetrahedral > monomeric octahedral. The  $\nu(Ni-N)$  frequency depends on the nature of the ligand comprising the connecting N-atom. *E.g.*, Me-NH<sub>3</sub>: 420-500 cm<sup>-1</sup> [23], Me-hydrazine: 306-440 cm<sup>-1</sup> [24], Me-glycine: 275-423 cm<sup>-1</sup> [25], Me-pyridine: 200-287 cm<sup>-1</sup>.

Sterically non-hindering substituents may influence the infrared spectra in two ways [16]:

(a) by their electric effects and

(b) by the alteration of the reduced mass.

Alkyl substituents hardly influence the  $\nu(Ni-N)$  frequency by means of their mass action. In accordance with their hyperconjugation effect, they donate electrons to the aromatic system, thus they increase the charge density at the N-atom and decrease the possibility of the  $t_{2g} - \pi^*$  charge transfer, as well as the bond order and the corresponding frequency. In accordance with the directive influence of alkyl groups, the change observed in 4-substituted compounds is larger than in 3-substituted ones. The substituents influence the  $\nu$ (Ni-X) frequency by means of similar effects.

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# CONVERSIONS OF TOSYL AND MESYL DERIVATIVES OF THE MORPHINE GROUP, XII\*

14-HYDROXY DERIVATIVES OF MORPHINE, III ISOTHIOCYANATO DERIVATIVES

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6-Deoxy-6-azido-14-hydroxyisocodeine and 6-deoxy-6-azido-14-acetoxyisocodeine were converted into the corresponding isothiocyanato derivatives with carbon disulfide in the presence of triphenylphosphine.

Intramolecular conversion of the intermediate isothiocyanato derivative obtained from 8-deoxy-8-azido-14-hydroxypseudocodeine under the conditions of the above reaction resulted in 2'-thiono-oxazolidino-(4',5' :  $8\beta$ ,14 $\beta$ )-8-deoxypseudocodeine.

The structures of the compounds prepared are verified by their synthesis, chemical conversions, as well as by their spectroscopic properties (IR, NMR).

In the course of an investigation of the conversions of the products obtained on nucleophilic substitution of tosyl and mesyl esters of morphine derivatives containing a hydroxyl group at the  $C_{14}$  position, the preparation of the corresponding isothiocyanato derivatives was attempted. In contrast with our observations on derivatives containing no substituent at  $C_{14}$  [1], 6-O-tosyl-14-hydroxycodeine could not be converted into the desired product with potassium thiocyanate in aprotic solvents (absolute acetone, methyl ethyl ketone, acetonitrile, dimethylformamide), in spite of the use of widely varied reaction conditions (mole ratio, temperature, reaction time).

The conversion of the amino derivatives of 14-hydroxycodeine [2] into 14-hydroxycodeine isothiocyanato derivatives with carbon disulfide [3] and thiophosgene [4] in alkaline medium could not be attempted because of the sensitivity of the molecule to the conditions of the reaction described in the papers mentioned. Therefore, the selected procedure was the method of treating an azide with carbon disulfide in the presence of triphenylphosphine, which ensures very mild reaction conditions [5].

In one of our previous papers [2] the preparation of 6-deoxy-6-azido-14hydroxyisocodeine (I) and 8-deoxy-8-azido-14-hydroxypseudocodeine (III) was described.

The reaction of I with carbon disulfide in the presence of triphenylphosphine yielded 6-deoxy-6-isothiocyanato-14-hydroxyisocodeine (II).

When III was allowed to react in the above manner, its intramolecularly cyclized derivative, 2'-thiono-oxazolidino- $(4^{\circ}, 5^{\circ}: 8\beta, 14\beta)$ -8-deoxypseudocodeine

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(IV) was obtained instead of the expected 8-deoxy-8-isothiocyanato-14-hydroxypseudocodeine. The structure of IV was confirmed by means of infrared spectroscopy (see the respective data of Table I).

Since in the latter case the isothiocyanato derivative cannot be prepared in the above manner, the synthesis of the derivative containing an isothiocyanato group at C-8 was attempted through the corresponding 8-azido-derivative of 14-acetoxycodeine.

In the azidolysis of 6-O-tosyl-14-acetoxycodeine (V), however, only one product was obtained, in spite of the widely varied reaction conditions also used in the case of 6-O-tosyl-14-hydroxycodeine [2]; this proved to be 6-deoxy-6azido-14-acetoxycodeine (VI). Its structure was verified by chemical and physical (IR) data. The deacetylation of VI gave 6-deoxy-6-azido-14-hydroxyisocodeine (I). The physical constants (m.p. and  $[\alpha]_D$ ) of the products obtained in two different ways were identical and the difference in the infrared spectra occurring in the case of C-6 and C-8 substituted products, C-6 = 940  $\pm$  10 cm<sup>-1</sup>, C-8 = 900  $\pm$  13 cm<sup>-1</sup>, could not be observed either.

6-Deoxy-6-isothiocyanato-14-acetoxy-isocodeine (VII) was prepared from VI by allowing it to react with carbon disulfide in the presence of triphenylphosphine.

The treatment of both 6-deoxy-6-isothiocyanato-14-hydroxyisocodeine and 6-deoxy-6-isothiocyanato-14-acetoxyisocodeine with ammonia in aqueous alcoholic medium [7] resulted in the same product, N-(6-deoxy-14-hydroxyisocodeinyl)-thiourea (VIII).

#### BOGNÁR et al.: TOSYL AND MESYL DERIVATIVES, XII



The identity of the products was also confirmed by infrared (and in the case of IV, by the NMR) spectra.

The physical constants and analytical data of the new compounds are summarized in Table I.

	Formula	М.р.,	p., [∝]D	An	alysis		TD .
. 12	Mol. wt.	°C		Calcd. %	Found %	-	IR
П*	$\mathbf{C_{19}H_{21}O_{3}N_{2}S}$	204	-182.7°	N 7.83	6.98	vOH	3400 cm <sup>-1</sup>
	357.446			S 8.97	8.39	$\nu N = C = S$	2060 cm <sup>-1</sup>
IV**	C19H21O3N2S	285-7	+120°	N 7.83	7.95	<b>vNH</b>	3076 cm <sup>-1</sup>
2 2	357.446		4. 1	S 8.97	8.77	vNH-C=S	I.1512 cm <sup>-1</sup>
						Sec. 1	II.1283 cm-1
		1			1		III.1173 cm <sup>-1</sup>
		i dente de				vC=S	714 cm <sup>-1</sup>
VI	$C_{20}H_{22}O_4N_4$	150-1	-316°	N 14.65	14.43	vOAc	1739 cm <sup>-1</sup>
-	382.402					vN3	2085 cm <sup>-1</sup>
			1-11-24			vOAc	1740 cm <sup>-1</sup>
VII	$\mathbf{C_{21}H_{22}O_4N_2S}$	163	-277°	N 7.03	6.65	vN=C=S	2108 cm <sup>-1</sup>
	398.466	1		S 8.04	8.32	νOH	$3400 \text{ cm}^{-1}$
VIII	$\mathrm{C_{19}H_{24}O_{3}N_{3}S}$	198-200	-320°	N 11.24	10.83	<b>vNH</b>	3320 cm <sup>-1</sup>
1	374.472			S 8.56	8.21	vH2N-C=S	1600 cm <sup>-1</sup>
	a start a second	2. 1 2.	10 10 10 10				

Table I

\* The infrared spectrum was recorded in 50 mg/ml chloroform solution. \*\*  $\nu C=S$  714 cm<sup>-1</sup> (latest literature data [9] assign  $\nu C=S$  at about 700 cm<sup>-1</sup>, contra-dicting KATRITZKY [10] who expects it at about 1170 cm<sup>-1</sup>). IV: NMR data:  $J_{8,NH} \sim 10.5$  Hz (JEOL 100, deuteropyridine solution).

## Experimental

#### 6-Deoxy-6-isothiocyanato-14-hydroxyisocodeine (II)

6-Deoxy-6-azido-14-hydroxyisocodeine (I) (1 g: 0.0028 mole) [2] was dissolved in carbon disulfide (15 ml); triphenylphosphine (0.73 g; 0.0028 mole) was added and the solution was refluxed for 2 hrs. The reaction mixture was evaporated to dryness and the solid residue suspended in anhydrous ether. The non-dissolved triphenylphosphine sulfide was removed by filtration (m.p. 156-159 °C). The filtrate was evaporated to dryness and the syrup residue crystallized from ether. The crystalline product was still contaminated with triphenylphosphine sulfide; this was removed by means of column chromatography (Silicagel G benzene: methanol = 8:2) to obtain 450 g (43.2%) of the product, m. p. 204° C;  $[\alpha]_D - 182.7^\circ$ (chloroform, 0.29).

C19H21O3N2S (357.446). Calcd. N 7.83; S 8.97. Found N 6.86, 6.98; S 8.38, 8.39%. IR:  $3400 \text{ cm}^{-1}$  (-OH); 2060 cm<sup>-1</sup> (-NCS).

#### 2'-Thionc-oxazolidino-(4',5'; : 8:14 )-8-deoxypseudocodeine (IV)

8-Deoxy-8-azido-14-hydroxypseudocodeine (III) (1.7 g; 0.005 mole) [2] was dissolved in carbon disulfide (25 ml) and after the addition of triphenylphosphine (1.32 g; 0.005 mole) the mixture was refluxed for 2 hrs. A crystalline substance separated during the reaction. The precipitate was filtered off and after evaporation of the carbon disulfide, the solid residue was extracted first with ether then with chloroform. The non-soluble portion was identical with the  $\begin{array}{c} \text{extracted inst with check then with choose of the instantial portion was identical with the product which separated from carbon disulfide (m.p., mixed m.p., TLC, analysis); 1.56 g (86.2%); [z]_D +120.7° (chloroform : ethanol = 2 : 1, 0.546). \\ C_{19}\text{H}_{210}\text{S}_{N2}\text{S} (357.446). \text{ Calcd. N 7.83; S 8.97. Found N 7.95, 8.09; S 8.73, 8.77\%.} \\ \text{IR: 3076 cm}^{-1} (\text{NH}); \quad \text{I. 1512 cm}^{-1} \\ \text{II. 1283 cm}^{-1} \\ \text{III. 1173 cm}^{-1} \end{array} \right\} (\text{NH}-\text{C}=\text{S});$ 

714 cm<sup>-1</sup> (C=S).

#### 6-Deoxy-6-azido-14-acetoxyisocodeine (VI)

6-O-Tosyl-14-acetoxycodeine (V) (5 g; 0.01 mole) [8] was dissolved in dimethylforma-mide (150 ml), and sodium azide (0.78 g; 0.012 mole) dissolved in water (8 ml) was added to it. The mixture was boiled on a hot water bath for 4 hrs. The reaction mixture was cooled, poured into water (750 ml) and extracted with  $3 \times 150$  ml of ether. The combined ethereal phases were washed with saturated sodium chloride solution ( $2 \times 50$  ml), dried over magnesium sulfate and evaporated to dryness. The residue was suspended in some anhydrous ether and filtered. The product was purified by recrystallization from a mixture of acetone and water to give 2.03 g (54.5%) of the product, m.p. 150-151 °C; [a]D-316° (chloroform, 0.5).

C20H22O4N4 (382.402). Calcd. N 14.65. Found N 14.43, 14.99%. IR: 1739 cm<sup>-1</sup> (-OAc); 2085 cm<sup>-1</sup> (-N<sub>3</sub>).

#### 6-Deoxy-6-isothiocyanato-14-acetoxyisocodeine (VII)

6-Deoxy-6-azido-14-acetoxyisocodeine (VI) (1.9 g; 0.005 mole) was dissolved in carbon disulfide (25 ml), and triphenylphosphine (1.32 g; 0.005 mole) was added to it. The solution was boiled for 2 hrs. The reaction mixture was evaporated to dryness and the residue suspended in anhydrous ether. The non-dissolved triphenylphosphine sulfide was removed by filtration. The ethereal filtrate was evaporated to dryness and the residue rubbed with anhydrous ether. The crystals which separated were recrystallized from a mixture of acetone and water to give

0.55 g (27.9%) of the product, m.p. 163 °C.  $[\alpha]_D - 277^\circ$  (chloroform, 0.41).  $C_{21}H_{22}O_4N_2S$  (398.466). Calcd. N 7.03; S 8.04. Found N 6.63, 6.65; S 8.32, 8.42%. IR: 1740 cm<sup>-1</sup> (-OAc); 2108 cm<sup>-1</sup> (-NCS).

#### N-(6-deoxy-14-hydroxyisocodeinyl)-thiourea (VIII)

(a) 6-Deoxy-6-isothiocyanato-14-hydroxyisocodeine (II) (780 mg; 1.95 mole) was refluxed in a mixture of 24% ammonia (7.68 ml) and ethanol (7.68 ml) for 3 hrs. On cooling a crystalline product separated which was purified further by recrystallization from aqueous ethanol to give 250 mg (30.6%) of the product, m.p. 193-200 °C; [a]D-320° (chloroform, 0.5).

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C<sub>19</sub>H<sub>24</sub>O<sub>3</sub>N<sub>3</sub>S (374.472). Calcd. N 11.24; S 8.56. Found N 10.81, 10.83; S 8.21, 8.15%. IR: 3400 cm<sup>-1</sup> (-OH); 3320 cm<sup>-1</sup>, 1600 cm<sup>-1</sup> thiourea.

(b) 6-Deoxy-6-isothiocyanato-14-acetoxyisocodeine (200 mg; 0.56 mmole) (VII) was refluxed in a mixture of 24% ammonia (2 ml) and ethanol (2.5 ml) for 3 hrs. The crystalline product which separated from the reaction mixture on cooling was recrystallized from aqueous ethanol.

As shown by its physical constants (m.p., mixed m.p., IR), the product was identical with the compound prepared according to (a).

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## INVESTIGATIONS IN THE FIELD OF SOLID STATE **POLYMERIZATION, XXIX\***

## INVESTIGATION OF SOLID STATE OLIGOMERIZATION OF ACENAPHTHYLENE INITIATED BY IODINE. STRUCTURE OF THE MONOMER AND OLIGOMERS\*\*

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The structure of acenaphthylene and the product of its solid state oligomerization initiated by iodine was investigated by X-ray analytical and infrared spectroscopic methods. Acenaphthylene crystallizes in the orthorhombic system with a space group Pba2. The lattice constants and the orientation of the molecules in the unit cells were determined.

The monomeric units in the oligomer molecules — showing a threo-di-isotactic configuration — are arranged along a helix with a twofold screw axis. The approximate size of the crystal grains built up from the oligomer chains has been determined. Comparison of the monomer structure with that of the oligomer has revealed that the oligomerization is possible by a relatively small motion of the acenaphthylene molecules, i.e. the crystalline phase controls the process, therefore, it is a topotactical reaction. This fact corresponds to the linear kinetic character described by us earlier.

In a previous publication [1] we reported on the iodine initiated solid state oligomerization. It has been established that the reaction can be described by a linear kinetic curve and the elementary reaction of initiation takes place via charge transfer complex formation between iodine and acenaphthylene followed by its dissociation into ions. An account will now be given of our studies concerning the structure of the oligomer formed and the topotactic character of the reaction.

Solid state polymerization may be accomplished essentially in two ways. In cases when the crystal structure permits linking of the molecules with each other through relatively small movements, the positions of the reacting monomer units during this movement, and also in the moment of coupling to the growing chain, are unambiguously fixed by the crystalline phase. This leads to a chain which has a regular structure correlating with the positions of the monomer molecules in the crystal lattice. This type of solid state polymerization is called topotactic. Should there be no possibility for this, the polymerization takes place in a new amorphous phase different from the monomer phase into which the molecules arrive by diffusion after emerging from their crystal lattice. In the course of this motion their position is random without being deter-

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mined by any definite controlling force, therefore, the polymer chain formed is also without any regularity. This type of reaction is referred to as 'topoatactic'. Examples of topotactic reactions are the solid state polymerization of cyclic compounds [2], cetyl vinyl ether [3], or cholesteryl acrylate [4]. A topoatactic process is the polymerization of N-vinyl succinimide [5].

Until recently the question of topotactic vs. topoatactic process was generally settled by kinetic methods. Namely, the former type was considered to correspond to a linear or decelerating conversion vs. time relationship and the latter type to an accelerating one. However, on the basis of more recent results and reassessment of the earlier data it seems likely that the formal classification is not always correct, and the character of the reaction should be settled in each case individually by comparing the results of structural and kinetic investigations [6] taking even the actual conversion into account.

#### Experimental

## Materials

Acenaphthylene was a 'Schuchardt' (München, Germany) product; its purification, properties, the conditions of oligomerization and the characterization of the product have been described elsewhere [1].

#### **Experimental** methods

The X-ray diffractograms were obtained on a Philips powder diffractograph using nickel filtered Cu—K radiation. The single crystal patterns were recorded on the instrument of the Central Research Institute for Chemistry, Hungarian Academy of Sciences, with nickel filtered Cu—K $\alpha$  radiation using a Buerger-camera; the precession angle was  $\mu = 30^{\circ}$ .

A Zeiss UR-10 type spectrophotometer was used for the I.R. investigation of the oligomers, the disks were made of 3-5 mg oligomer and 1 g potassium bromide. The wavenumber accuracy of the spectra is 10 cm<sup>-1</sup>.

## **Results and discussion**

The diffractograms obtained are characteristic of ordered, crystalline products. To establish a possible correlation between the structure of the starting material and the end-product a detailed analysis of both was necessary.

For determining the crystal structure of the monomer, single crystals have been prepared by diffusive crystallization applying an alcohol-water solvent-nonsolvent system. Buerger camera photographs in accordance with the three axes were taken. It has been established from the projections that the material crystallizes with orthorhombic symmetry, its lattice constants are: a = 7.70 Å; b = 7.85 Å; c = 14.11 Å. The unit cell contains 4 molecules.

COHEN [7] has recently reported crystallographic data of acenaphthylene. It is obvious that the space group symbols (Pba2<sub>1</sub>, Pbma) cannot be correct and there are some small differences concerning also the unit cell dimensions.

The density calculated from the cell dimensions  $-1.182 \text{ g/cm}^3$  - agrees with the value which has been measured by us (1.176 g/cm<sup>3</sup>).

#### **Packing considerations**

The study of systematically absent reflections (h01: h = 2n + 2, 0k1: k = 2n + 1) indicates the possibility of two space groups: Pba2 or Pbam (No. 32 or 55). The symmetry relations required by these together with the dimensions of acenaphthylene — taken as a first approximation equal to those of acenaphthene [8] — require that the symmetry axis of the molecules corresponds to the the crystallographic c axis. As a consequence of this, the molecules must be in special position and, on the other hand, the structure cannot belong but to the Pba2 space group. In such a special position the symmetry permits only two molecules. The intensities of 001 reflections are very weak when



Fig. 1. Electron density map of acenaphthylene projected on h01

l = 1, 2 and 3. Therefore, it has to be assumed that the other two molecules belonging to the unit cell are repeated in the direction of the *c* axis within approximately one half period. The fact that the distance between two molecules must be at least the van der Waals radius (3.5 Å) implies that the X and Y coordinates of the molecules in the layers, one beneath the other, cannot be equal, *i.e.* two molecules cannot be located immediately under one another but are shifted along the *a* or *b* axis with one half of a cell dimension. Furthermore, this means that the angle between the plane of the perinaphthylene rings and the *a* axis in a certain layer is approximately the same as that corresponding to the *b* axis in the layers beneath and above. Because of the fact of oligomerization, it has to be supposed that the vinyl groups of the acenaphthylene molecules in two neighbouring layers are directed towards each other.

The first Fourier maps obtained from the phases of structure factor calculations based on packing considerations are presented in Figs 1 and 2:

$$R_{h01} = 0.26, \ R_{0k1} = 0.4$$
.

Calculations for the exact description of the structure are in progress;\* the above structure is shown in Fig. 3. The heavy lines designate the unit cell and the symmetry elements. Medium contour lines are used to indicate molecules of the upper layer and a thin line gives the backbone of the molecules



Fig. 2. Electron density map of acenaphthylene projected on 0k1



Fig. 3. Crystal structure of acenaphthylene

in both layers. The concept shown in the figure has been verified with a threedimensional Fourier-diagram.

## Structure of the oligomer

The X-ray diffractogram of the product obtained in iodine initiated solid state oligomerization is shown in Fig 4. From this two essential conclusions can be drawn concerning the structure of the oligomer: the product is crystalline and its structure preserves certain elements of the monomer structure.

\* F. CSER, K. SASVÁRI; to be published in Acta Chim. Acad. Sci. Hung.



Fig. 4. X-ray diffractogram of acenaphthylene oligomer

Quantitative evaluation of the diffractograms makes possible to ascertain even finer details. From the half-peak width of the diffraction lines the ranges of regularity for the material can be determined. The spacings corresponding to the diffraction lines, the ranges of regularity calculated from the half-peak width as well as the correlation between the face indices of the crystal and the lines are summarized in Table I.

100	100
	-00
20	102
20	020
15-17	
	$20 \\ 15 - 17$

 
 Table I

 Characteristic data of the crystalline oligomer of acenaphthylene formed in solid state under the influence of iodine

Three further reflections can be recognized on the more detailed diffractogram with line widths corresponding to 100-150 Å ranges of regularity.

Among the lines found on the diffractogram the d = 3.9 Å one has the highest intensity, the 3.9 Å identity period must be specific to the majority of the atoms building up the chain molecules. This is conceivable theoretically either as an interchain or as an intramolecular identity. However, in the case of chains with side groups, as the acenaphthylene oligomers, such a small intermolecular identity period is impossible. Hence, this line is due not to the highly ordered array of the chain molecules but to repetition within the chain itself. Supposing the possibility of stereoisomerism owing to two different configurations of the monomer unit in the polymer chain, four kinds of regular chain structures are theoretically possible: *erythro*- and *threo*-, diiso or di-syndiotactic. But it follows from the structural parameters of the acenaphthylene molecule that only *threo*-diiso or *threo*-di-syndiotactic regular chain can be formed.

Erythro chains cannot be imagined because diisotactic chain propagation would lead to the formation of a self-terminated cyclic trimer or tetramer. On the other hand, the corresponding di-syndiotactic polymer chain is impossible owing to the significant steric hindrance caused by the 1,8-perinaphthylene ring.



Fig. 5. Two possible types of the acenaphthylene polymer chain with ordered structure

From the two possible regular structures the *threo*-diisotactic spiral chain corresponds to a helix and the *threo*-di-syndiotactic arrangement results a stair-stepped rigid rod. In the case of the first, in accordance with the two possible configurations of the monomer units, a right- or left-handed helix may be formed. If only left- or only right-handed helices were formed, the product would rotate the plane of polarized light, therefore, the structure of such chains could be proved by measuring the optical activity. However, since the present system contains no asymmetric catalyst, the formation of helices with both chiralities is equally probable. Hence, the experimental fact that the products are optically inactive does not mean a rod-like structure with *threo*-di-syndiotactic arrangement. This effect of course cannot be the result of compensation between units linked together in one oligomer molecule. Compensation between whole oligomer molecules is rather more likely since within one chain configuration only the same kind can exist, the rotation about the C—C bonds of the main backbone being sterically hindered.

The two possible types of chain with ordered structures are shown in Fig. 5.

Stereochemical considerations alone also indicate that the product corresponds to the *threo*-diisotactic structure.

The stair-stepped structure formed due to the di-syndiotactic arrangement must be limited to blocks of not more than 3-4 units because of the

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presence of rigid, bulky side groups, while this steric hindrance does not act in the case of a helical structure. This supposition is corroborated by the fact that compounds containing aromatic rings generally form regular structures. Namely, the rings are located in parallel at a distance of  $3.4 \pm 0.1$  Å from each other, an arrangement very easily realized in a helical form.

Further evidence in favour of the above structure has been obtained by infrared spectroscopy.

As indicated in Fig. 5 the two hydrogens linked to the tertiary carbon atoms in 1.3 position have different steric anellations in the two types of struc-



Fig. 6. Characteristic part of the I. R. spectrum of the oligomer formed in solid state

tures. This permits to distinguish between the latter on the basis of the infrared spectra [9]. These hydrogens in a diisotactic structure are 1.3-axial (a,a), while in a di-syndiotactic one, 1.3-equatorial (e,e). Similar positions are occupied by the hydrogens in *cis*- and *trans*-decalin with the chair configuration. The direction of the bond in the two C—H groups linked to the spot of anellation in *cis*-decalin is *a*,*e* anelled, while in *trans*-decalin *e*,*e* anelled. The anellation of *cis*-decalin does not fit exactly to that of the diisotactic polymer chain but the given analogy is known as the best, and this difference does not influence the conclusions concerning the interaction of the above hydrogens with the protons of the perinaphthylene ring. Thus the infrared spectra give a possibility for choice between the two oligomer structures.

The significant range of the infrared spectrum for the product obtained in iodine initiated solid state oligomerization is shown in Fig. 6. A strong absorption is observed at 2905—2911 cm<sup>-1</sup>. This corresponds to the asymmetric  $CH_2$  stretching in *cis*-decalin at 2924 cm<sup>-1</sup>[10] but the restricted chain mobility in *oligo*-acenaphthylene and, therefore, the reduced interaction energy of the 1.3-hydrogens may cause some decrease in the frequency. The presence of this band means 1.3-axial position for the aliphatic hydrogens of the polymer chain and a lack of interaction with the protons of the relatively distant perinaphthylene rings. In *trans*-decalin the same vibration appears at 2857 cm<sup>-1</sup> [10], the significant downward shift can be attributed to the 1.3-equatorial hydrogens interacting with the hydrogens of the ring. There is no absorption at this frequency in the spectrum of the oligomer.

In the case of *cis*-decalin the symmetric C—H stretching vibration band is at 2841 cm<sup>-1</sup>. In the spectrum of the oligomer the C—H stretching vibration band can be found at the same frequency but, owing to the proximity of a strong absorption band, it shows only as a shoulder.



Fig. 7. Structure of the helical oligomer chains with a 2-fold screw axis

The evidence presented above supports the assumption that the oligomer chains formed in the solid state under the influence of iodine are *threo*-diisotactic, *i.e.* have a helical structure.

Theoretically, the helix may have a 2, 3, 4, 6, 8-fold, etc., screw but in practice the 2, 3, 4- and 6-fold screw axes are usual. If one attempts to build up the polymer chain of acenaphthylene, even a 3-fold axis would mean such significant bond angle deformations that the possibilities of 4- or 6-fold axes can safely be neglected. A 2-fold screw axis seems to be most probable for the helix, as the corresponding structure shows in Fig 7. This is favoured by the fact that its formation requires relatively small movement of the molecules in the orthorhombic crystal, and that this permits the optimal packing coefficient and the bond angles to remain nearly free of distortions.

The only argument against this is the distance between the aromatic planes which is about 3.1 Å in the case of a 2-fold axis. However, since the

angle between the plane of the molecules and the axis of the helix deviates from 90°, according to our calculations it is about 60°, the interatomic distances will not be less than the value required by the van der Waals range (3.4 Å). A 3-fold axis is not likely because, to form the corresponding helix, the monomer molecules must be moved extensively from their original positions in the crystal lattice. The structure specified by the 2-fold screw axis is also supported by the density determinations.

On the basis of the dimensions calculated from the half peak width of the diffractogram, the crystal grains of the oligomer can be visualized as 100-150 Å wide and 20 Å thick sheets. The helical chain molecules are perpendicular to the plane of the sheet, their axes coinciding with the nearly equivalent a or b axes of the monomer. Within the sheet the helices are located at distances of 6.7 Å and 7.6 Å from each other along the two perpendicular directions, respectively.

In order to obtain further information on the structure, the U.V. spectrum of the oligomer has also been investigated. The wavelengths and relative intensities referred to the 324 nm bands are given in Table II.

Location of band (nm)	Relative intensity	Location of band (nm)	Relative intensity
285	1.07	324	1
297	1.12	344	0.59
304	1.5	365	0.81
310	1.46	385	1.4
318	1.02	408	1.54

#### **Table II**

Typical U.V. absorption bands and their relative intensities for oligo-acenaphthylene formed in solid state under the influence of iodine

Since no correlation was found between the individual bands and the structural units of the molecule, the spectrum was not suitable for verifying the structure. However, interesting qualitative observations can be made by comparing the U.V. spectrum with those of polymers obtained by high energy initiated solid state polymerization and with the spectra of di- and tetramers of acenaphthylene reported by MUELLER [11]. As can be established, the locations of the bands appearing in the spectrum of the oligomer are identical with those of fluorocyclene but the intensity ratios are different. One range of the oligomer spectrum (285—324 nm) is similar to those of the polymers and the di-acenaphthyl-cyclobutanes, while the other (344—408 nm) is in good agreement with the fluorocyclene and the di-acenaphthylidene spectra.

On the basis of these data it can be established that the structure of the oligomer as well as the location and quality of its chromophores do not correspond completely either to the product of radiation initiated polymerization or to the di- or tetramer but show a great similarity to them in some details. It is more descriptive to say that the polymer prepared in solid state by high energy radiation retains the position and arrangement of the perinaphthylene rings





Fig. 8. Characteristic part of the I.R. spectrum of poly-acenaphthylene produced by Ziegler-Natta catalysis

Fig. 9. Characteristic part of the I.R. spectrum of poly-acenaphthylene produced with titanium tetrachloride

present in di-acenaphthylene and fluorocyclene and the U.V. spectrum of the oligomer is a combination of these features.

For comparison the structure of oligomers produced in liquid state in connection with high molecular weight polymers has also been investigated. (The latter were obtained in solution with a Ziegler-Natta catalyst and titanium tetrachloride at the Polyolefin Department of the Research Institute for Plastics, Budapest.)

The spectra of the high molecular weight products (see Figs 8 and 9) indicate a complex character of the polymer chains. Besides the bands corresponding to *cis*-decalin (2924 cm<sup>-1</sup> and 2841 cm<sup>-1</sup>) one band of *trans*-decalin (2857 cm<sup>-1</sup>) can be recognized too. This, in the case of poly-acenaphthylene, would imply a *threo*-di-syndiotactic structure. Hence, in the polymer formed in liquid state, units with both configurations are present but the method does not distinguish between random distribution or longer microblocks. Concerning this problem essential proof is offered by the X-ray diffractograms

of the above polymers (Figs 10 and 11). These diffractograms contain only two of those powder lines (d = 5.3 Å and d = 3.9 Å) which can be found in the oligomer prepared in solid state. Even these two lines have a spreaded, amorphous-type profile, with ranges of regularity calculated from the half-widths



Fig. 10. X-ray diffractogram of poly-acenaphthylene produced by Ziegler-Natta catalysis



Fig. 11. X-ray diffractogram of poly-acenaphthylene produced with titanum tetrachloride

equal to not more than 2—4 periods. For the polymer prepared by Ziegler-Natta catalysis another line with a spacing of d = 11.0 Å can also be identified, showing a width corresponding to about three periods as range of regularity. The products of liquid state oligomerization initiated by iodine in *n*-heptane or dichloroethane give diffractograms identical with that of the high molecular weight polymer prepared with titanium tetrachloride (Fig 11).

The structure of the product formed in the iodine initiated solid state oligomerization as well as the fact that this process can occur without significant movement of the monomer molecules from their position in the crystal

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lattice, prove the process to be topotactic in character. This means that in the present system the linear kinetic behaviour reported in a previous communication [1] is indeed the consequence of topotacticity.

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## RECENSIONES

M. VON ARDENNE, K. STEINFELDER und R. TÜMMLER: Elektronenanlagerungs-Massenspektrographie organischer Substanzen

#### Springer-Verlag, Berlin, 1971. S. 403 + VIII.

Auf dem Gebiet der organischen Massenspektroskopie zeigt sich — parallel mit der Verbreitung dieser Methode — steigendes Interesse für die Anwendung speziellerer bzw. schonenderer Ionisationsverfahren (Photoionisation, Feldionisation, chemische Ionisation, Elektronenanlagerungs-Ionisation) zur Ergänzung der Elektronenbombardierungstechnik. Deshalb halte ich es für besonders zeitgemäß, daß dieses Buch jetzt erschienen ist, geschrieben von Verfassern, die über hervorragende Kenntnisse in der Entwicklung und Anwendung der wenig bekannten Methode der Elektronenanlagerungs-Massenspektrographie verfügen.

Der erste Teil des Buches behandelt die theoretischen Grundlagen und methodischen Fragen der Elektronenanlagerungs-Massenspektrographie. Die von den Verfassern gebauten Apparaturen und die Technik der Datenverarbeitung werden ausführlich diskutiert. Das Verständnis des Buches erfordert keine besonderen Vorkenntnisse des behandelten Gebietes, weil das Buch auch viele Einzelheiten enthält, die auch in manchen anderen Fachbüchern über Massenspektroskopie zu finden sind (z. B. die Auswertung von Photoplatten) und die den Umfang des Buches steigern. Jedoch enthalten auch diese Teile zahlreiche »Kunstgriffe«, kleine, auf unmittelbaren Erfahrungen beruhende Hinweise, die in der Praxis von Nutzen sein können.

In den weiteren Abschnitten des Buches - in Einklang damit, daß die Ionisationsmethode durch Elektronenanlagerung vor allem negativ geladene Ionen liefert — findet man im wesentlichen die Beschreibung der Massenspektren negativer Ionen. Die Verfasser beschäftigen sich kurz mit den möglichen Mechanismen der Bildung negativer Ionen (Resonanzanlagerung, dissoziative Resonanzanlagerung, Fragmentierung, Ion-Molekül-Reaktionen) und geben einen Überblick über die Anwendungen (Molekulargewichtsbestimmung, Strukturaufklärung) bei verschiedenen Gruppen organischer Verbindungen und Stoffmischungen. Ein umfangreiches Kapitel führt auf systematische Art die Massenspektren zahlreicher Verbindungen vor und gibt ihre Deutung an. Dieser zweite Teil des Buches, den Anhang mit inbegriffen, bringt eine einzigartig hohe Zahl an neuen Negativionen-Massenspektren. (Im Anhang werden die Elektronenanlagerungs-Massenspektren und die Massenzahlen der wichtigeren Ionenspitzen für mehr als 700 organische Verbindungen angegeben.) Diese Spektren verleihen dem Buch einen besonders hohen Wert. Dagegen ist die Diskussion, besonders die Art der Beleuchtung der Zusammenhänge zwischen dem Massenspektrum und der Struktur auf einem ziemlich niedrigen Niveau gehalten. Auch ist zu bedauern, daß die Ladung des Molekülions in den Liniendiagrammen nicht konsequent angegeben ist. Dies ist deshalb besonders störend, weil das Buch nicht nur Negativionen-Massenspektren behandelt.

Infolge der zahlreichen Beispiele und systematischen Angaben eignet sich das Buch dazu, dem Leser einen Überblick über die wenig bekannte Methode der Elektronenanlagerungs-Massenspektrographie und über ihre Anwendungsmöglichkeiten in der organischen Strukturforschung und in der Lösung analytischer Probleme zu geben. Das Buch überzeugt den Leser davon, daß diese Ionisationsmethode — obwohl sie im allgemeinen gegenüber der verbreiteten Ionisationstechnik der Elektronenbombardierung nicht konkurrenzfähig ist — infolge der schonenderen Art der Ionisation in einem ziemlich breiten Kreis von Substanzen über wesentliche Vorteile verfügt.

J. TAMÁS

Handbuch der analytischen Chemie Hrsg. von W. FRESENIUS und G. JANDER Bd. III a α 1: Elemente der dritten Hauptgruppe Bor. 2. Aufl.

Bearb. von G. Wünsch und F. Umland. Mit 45 Abb. XVI + 186 Seiten

Springer Verlag, Berlin-Heidelberg-New York, 1971

Der neueste Band der Serie widerspiegelt getreu jene Entwicklung, die einerseits in der analytischen Chemie und andererseits in der Bor-Chemie stattfand. Dies gilt besonders für die Abschnitte 3 und 4 des Buches, in welchen die Trennverfahren und die Bestimmungsmethoden beschrieben werden.

Nach einem kurzen zusammenfassenden Überblick über die allgemeinen analytischen Reaktionen, Trennverfahren und Bestimmungsmethoden des Bors befaßt sich Abschnitt 2 mit der Probenvorbereitung. Die Qualität der zur Borbestimmung verwendbaren Gefäße (2.1), die Verflüchtigungstendenz der Borsäure beim Kochen, Eindampfen und Mineralisieren bzw. die Vermeidung der bei der Vorbereitung eventuell auftretenden Fehler (2.2) bilden das Rückgrat dieses Teiles. Hier wird auch ein Überblick über die Verfahren zur trockenen und nassen Mineralisation biologischer Substanzen sowie über die Methoden zum Aufschluß gegeben (Abschnitte 2.3 und 2.4).

Unter den Trennverfahren (Abschnitt 3) werden die auf der Destillation von Borsäuremethylester, auf Ionenaustausch und Extraktion beruhenden Methoden beschrieben. Dieser Abschnitt behandelt die Trennung von Borsäure-methylester mittels Mikrodiffusion sowie pyrohydrolytische Trennung von Bor, ferner die Entfernung der störenden Ionen durch Elektrolyse und Fällung.

In dem sich mit den Bestimmungsmethoden befassenden Abschnitt 4 behandelt das Buch, nach Beschreibung der wenigen gravimetrischen Methoden, eingehend die volumetrischen, fluorimetrischen, flammenphotometrischen sowie spektralanalytischen, radiochemischen und polarimetrischen Bestimmungsmöglichkeiten, unter Angabe der verschiedenen Arbeitsmethoden. Es wird ein kurzer Überblick über die Anwendungsmöglichkeiten der neuestens entwickelten thermometrischen, atomabsorptionsspektrophotometrischen, massenspektrometrischen sowie über die auf Röntgenfluoreszenz und Anwendung der Elektronenstrahl-Mikrosonde beruhenden Methoden zur Borbestimmung gegeben.

Abschnitt 5 beschreibt die Bestimmung von Bor an einigen konkreten Stoffen (Fluorwasserstoff und Fluoride, Germanium und Germaniumverbindungen, Glas, Silicium und Siliciumhalogenide, Stahl, Titan). Der letzte Abschnitt 6 gibt über die Bestimmung einiger spezieller Borverbindungen (Phenylborsäuren, Borwasserstoff-Verbindungen) Auskunft.

Die Verfasser berücksichtigten die Literatur praktisch bis 1970, deren Angabe den Lesern viel Mühe erspart. Die Verwendung dieses Werkes wird durch das sehr detaillierte, gut übersichtliche Inhaltsverzeichnis erleichtert.

E. BODOR

## Proceedings of the 3rd Symposium on Coordination Chemistry

Vol. 2. Plenary lectures and discussion of contributed papers. Akadémiai Kiadó, Budapest. Edited by Mihály T. BECK. 287 pages

The first 165 pages of the book contain the text of the reviews forming the basis of the five plenary lectures held at the 3rd Symposium on Coordination Chemistry, Debrecen 1970.

J. BJERRUM discusses the equilibria of formation of inner and outer sphere type complexes. D. N. HUME's lecture deals with the use of electronic computers for the determination of the equilibrium stability constants of mixed ligand complexes. H. DIEBLER discusses the kinetics of the elementary steps of metal complex formation. The paper of YA. D. FRIDMANN treats the rules of the formation of mixed complexes. Finally, A. E. MARTELL lectures on the metal chelate mechanism of organic reactions in mixed ligand complexes.

Thus, the papers deal without exception with the actual problems of coordination chemistry, of great interest today. The authors, well-known experts of the individual subjects, also illustrate the topics discussed by new results in the respective fields.

At the end of each paper, a detailed list of references is given, which makes the volume a useful handbook for those who wish to orient themselves in the relevant literature.

#### RECENSIONES

The second part of the book gives on more than 120 pages the full discussion of the papers presented at the 3rd Symposium on Coordination Chemistry. In the case of several papers, it gives in the form of short communications, supplements to the papers published in the first volume of this book, made available before the Symposium to the participants. These short papers are followed by the full discussion material, the answer of the authors included. The discussion of each paper is followed by a list of references.

In accordance with the sphere of theme of the Symposium, the new results presented are primarily concerned with mixed complexes, polynuclear and outer sphere type complexes, giving valuable information to those interested in coordination chemistry.

The publication (together with its first volume) covers a wide field of very up-to-date knowledge in coordination chemistry. The discussion part reflects opposite views concerning some of the problems, and in certain cases the mode of reconciling the differences.

Among the lecturers and the contributors to the discussion there are many names of international renown, such as S. AHRLAND (Thermodynamics of the formation of outer sphere complexes), S. KIRSCHNER (Optically active complexes), P. KRUMHOLZ (Dissociation mechanism of metal chelates), J. J. STEGGERDA (Cobalt(III) mixed complexes), M. L. GOOD (Mössbauer investigation of mixed complexes), F. J. C. ROSSOTTI (Determination of stability constants), and many others.

Owing to the wide and modern information presented, the book will be of interest and use not only to researchers in the field of coordination chemistry, but also to inorganic chemists and biochemists working in interdisciplinary fields and interested in coordination chemistry, and to those teaching general chemistry at university level.

K. BURGER

## A. ZLATKIS and V. PRETORIUS (editors): Preparative Gas Chromatography

#### Wiley Interscience, New York, 1971, 402 pages

The great efficiency of gas chromatography provides new possibilities not only in analysis, but also in the separation of complex mixtures and in the preparation of high-purity materials. In the recent years, besides laboratory-scale applications, extensive research work has been started to solve the scale-up problems in preparative gas chromatography and to introduce it as an industrial "production" method.

In the last decade a great number of papers have dealt with the investigation of theoretical and practical problems of preparative gas chromatography. In manuals and monographs dealing with this method, the preparative applications of gas chromatography are also discussed to some length; however, the present book is the first comprehensive work aiming at a general survey and evaluation of this extremely important field.

The book consists of ten chapters written by the best experts of the various special fields discussing theoretical, realization and application problems of preparative gas chromatography.

In Chapter 1 (Basic Theory; PRETORIUS, V. and DE CLERK, K.; 53 pages) the theoretical fundamentals of gas chromatography are summarized. The mathematical relationships are reviewed in relation to a relatively simple model and only to a limited extent which is necessary for the further application. The factors affecting the processes taking place in the preparative apparatus and the problems of scale-up are assessed on the basis of theoretical considerations.

Chapter 2 (Inlet System; HUPE, K. P.; 17 pages) deals with the different systems applied for the introduction of liquid samples. The possibilities of the introduction of maximum 10-ml samples are discussed only; the problems arising with larger samples are not considered.

Chapter 3 (Preparative Column Technology; PECSAR, R. E.; 68 pages) comprises the evaluation methods of column operation, based on the theoretical fundamentals treated in Chapter 1. The effects on the efficiency of various factors are discussed in detail, such as sample size, injection technique, column packings, preparation of the column, interconnecting elements and the operational parameters.

Chapter 4 (Outlet System; HUPE, K. P.; 19 pages) summarizes the methods and devices used for the effective trapping, collection and detection of the components separated. Similarly to Chapter 2, the elution and collection of only small quantities (a few ml) are considered.

In Chapter 5 (Programming Process and Automatic Control; BUSCH, V.; 23 pages) the basic aspects of operation and control and the most important constructions of automatic laboratory preparative gas chromatographs are discussed. A more detailed description of the practical solutions would have been desirable here. Chapter 6 (Temperature and Flow Programming; KAISER, R.; 23 pages) deals with the possibilities and results of temperature and flow programming in preparative columns.

In Chapter 7 (Applications in Organic Chemistry; VERZELE, M.; 22 pages) the application possibilities of preparative gas chromatography are discussed in the separation of various organic compounds. The operation and capacity of long columns with small diameter are compared with those of short columns having larger diameter, as regards their efficiency in different separation problems. Several chromatograms are shown to illustrate the possible applications.

The first part of Chapter 8 (Applications in Flavor Research; MERRITT, C.; 41 pages) summarizes the separation methods applied in the research of flavor and aroma components. In the second part the possibilities of gas chromatographic separation are discussed. The investigation of flavor compounds can be considered a special area of micro-preparative gas chromatography because of the small amounts of the components ( $\mu$ g) and the difficulties arising in the separation of samples containing a large number of compounds with different molecular weights and chemical structures. Several examples are given to illustrate the separation problems; usually the application of several stationary phases, occasionally of capillary columns is required.

The introductory part of Chapter 9 (Biochemical and Biomedical Applications of Preparative Gas Chromatography; VANDEN HEUVEL, W. J. A. and KURON, G. W.; 47 pages) reviews the possibilities of gas chromatography in the separation and purification of compounds of biological interest and their derivatives. Combination of gas chromatography with mass spectrometry, as well as the separation of labelled compounds and radioactive detection methods applied for their direct investigation are discussed. After a short survey of the operational conditions of gas chromatographic separation, some examples are given for the illustration of the separation of steroids, lipids and other compounds and the identification of the products obtained.

The topic of Chapter 10 (Continuous Chromatographic Techniques; BARKER, P. E.; 69 pages) is the use of gas chromatography as a continuous unit operation and the different ways of its realization. One important technique involves the moving-bed processes; their operational characteristics and possible applications are discussed in detail. The second main group treated comprises the circular (rotating) column techniques and apparatuses developed by the author and his co-workers. The applications and the efficiency of the techniques are illustrated by several practical examples. Other methods are discussed as the third group. Finally, batch and continuous methods are briefly compared.

The book contains a total of 611 references given at the end of the individual chapters. A well-constructed, detailed subject index greatly facilitates the use of the book.

The book is a very useful manual for those interested in the preparative applications of gas chromatography. Furthermore, it provides valuable informations for the separation and identification of different compounds in research and development in the fields of organic chemistry, food chemistry, pharmaceuticals, biochemistry, biomedical and related areas.

L. SZEPESY

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73.74014 Akadémia Nyomda, Budapest – Felelős vezető: Bernát György

## АСТА СНІМІСА том 75 – вып. 3

РЕЗЮМЕ

## Некоторые химические реакции электродной дуги и их роль в спектрохимическом анализе, Х

#### Исследование реакции кислород — азот

3. Л. САБО и И. ТОТ

Был разработан метод определения количества окисей азота, образующихся в дуге. С помощью данного метода было доказано, что первоначально в дуге образуется моноокись азота, количество которой, однако, зависит от других реакций дуги — в первую очередь, от реакции образования двуокиси углерода —, оказывающих влияние на соотношение кислорода и азота. С увеличением силы тока зона реакции кислорода и азота почти линейно возрастает.

## Анноннообменные свойства урана, присутствующего наряду с микрограммовыми количествами нонов других металлов, в Wofatit—SBU

Использование для аналитических целей уксусной, гликолевой, тиогликолевой, янтарной, яблочной и тиояблочной кислот в качестве комплексообразователей

О. ГЮРТЛЕР, ХУ-КСУАН-АНХ и Х. ХОЛЫ (АПФЕЛЬ

Были изучены ионообменные свойства урана, находящегося совместно с микроколичествами тория(IV) и ионами других металлов, в присутствии уксусной, гликолевой, тиогликолевой, янтарной, яблочной и тиояблочной кислот при различных pH. Описывается отделение урана(IV) с помощью адсорбционной хроматографии на колонке, в присутствии тиогликолевой кислоты. Были определены коэффициенты распределения U(IV), Th(IV), Mo(VI), Fe(II), Fe(III), Se(III), Y(III), Mg(II), Ca(II), Sr(II) и Ba(II) в пристуствии вышеописанных кислот, при pH = 2,5 и 4,0, на WOFATIT-SBU и SBW.

## Ректификация многокомпонентных смесей, III

Локальные закономерности траекторий процесса непрерывной ректификации при конечных флегмовых числах

л. А. СЕРАФИМОВ, В. С. ТИМОФЕЕВ и М. И. БАЛАШОВ

В работе исследованы локальные закономерности в поведении траекторий процесса ректификации в окрестности стационарных точек при конечных флегмовых числах. Показано, что динамической системе ректификации присущи стационарные точки только типа «узел» и «седло». Проанализированы различные случаи стационарности в исследуемой системе. Анализ проведен на модели идеального противотока при условии равенства частных коэффициентов массоотдачи для всех компонентов в каждой из фаз. Для зеотропных смесей, в диаграммах которых отсутствуют линии  $\alpha_{ij} = 1$ , приведена общая картина хода траекторий процесса непрерывной ректификации. Выявлен качественный ход линий стационарности в концентрационных симплексах.

## Ректификация многокомпонентных смесей, IV

Нелокальные закономерности траекторий процесса непрерывной ректификации трехкомпонентных смесей при конечном флегмовом числе

л. А. СЕРАФИМОВ, В. С. ТИМОФЕЕВ и М. И. БАЛАШОВ

В работе исследованы нелокальные эакономерности траекторий процесса ректификации при конечных флегмовых числах на примерах неидеальных трёхкомпонентных смесей, содержащих азеотропы. Выявлены основные закономерности формирования областей ректификации при переменном флегмовом числе.

Определены линии предельно возможных составов конечных продуктов (дистиллята и кубового продукта).

Установлено, что при изменении флегмового числа области ректификации могут изменять конфигурацию. Выявлены закономерности зарождения и развития областей ректификации при переменном флегмовом числе.

## Изучение адсорбционных явлений на платиновом электроде с помощью радиоактивной техники, XII

#### Исследование адсорбции н-пропанола

дь. хорани и м. новак

Адсорбция н-пропанола изучалась на платинированном платиновом электроде с помощью радиоактивной техники. Было установлено, что происходит необратимая хемосорбция, которая не может быть охарактеризована равновесной изотермой. Кажущаяся зависимость между концентрацией и потенциалом, по всей вероятности, вызвана различными окислительными-восстановительными реакциями.

## Спектрофотометрическое исследование реакций 2,3-дихлор-5,6-дицианп-бензохинона с различными донорами

#### Р. Д. СРИВАСТАВА и Г. ПРАСАД

Спектрофотометрически были исследованы реакции взаимодействия 2,3-дихлор-5,6дициан-п-бензохинона с аценафтеном, дифениламином и о-толуидином. На основе результатов было установлено, что во всех случаях вначале наблюдаются полосы пз, исчезновение которых происходит симультанно с появлением полосы в области 340 мµ. Природа и происхождение этой полосы приписывается продуктам реакции.

## ИК спектры комплексов никеля (II) с пиридином, пиколином и лутидином

#### Й. ЧАСАР

Приводятся ИК спектры комплексов Ni(pi)<sub>2</sub>X<sub>2</sub> и Ni(pi)<sub>4</sub>X<sub>2</sub> (X = Cl<sup>-</sup>, Br<sup>-</sup>), а также Ni(4-Y-pi)<sub>4</sub>Cl<sub>2</sub> (Y = метил, этил, пропил, винил; *з-метил*) в области 375–8750 см<sup>-1</sup>. Было установлено, что деформационные колебания «в плоскости» и «вне плоскости» кольца аро-

матического лиганда в области 610 и 410 см<sup>-1</sup>, а также колебания  $\nu$ (Ni–N) и  $\nu$ (Ni–X), обнаруживаемые в области низких энергий, могут быть использованы для определения геометрии молекулы.

## Исследование тозиловых и мезиловых производных в ряду морфина, XII

Производные 14-гидроксиморфина, III. Изоцианатные производные

Р. БОГНАР, Т. МИЛЕ, Ш. МАКЛЕЙТ и Ш. БЕРИНИ

Из 6-дезокси-6-азидо-14-гидрокисиизокодеина, а также 6-дезокси-6-азидо-14-ацетоксиизокодеина с помощью дисульфида углерода в присутствии трифенилфосфина, были получены соответствующие изотиоцианатные производные.

Изотиоцианатные производные, образующиеся в качестве промежуточных продуктов из 8-дезокси-8-азидо-14-гидроксипсевдокодеина, в условиях вышеупомянутой реакции претерпевают интрамолекулярную перегруппировку с образованием 2'-тионо-оксазолидино-(4',5' : 8β, 14β)-8-дезоксипсевдокодеина.

Структура полученных соединений подтверждалась на основе метода их образования, реакций их химических превращений, а также на основе их спектральных свойств (ИК и ЯМР).

## Исследования в области твердофазной полимеризации, XXIX

Исследование твердофазной олигомеризации аценафтилена, инициированной йодом. Строение мономера и олигомера

ДЬ. ХАРДИ, Г. КОВАЧ, Ф. ЧЕР и ДЬ. КОСТЕРСИТЦ

С помощью рентгено-аналитического и ИК-спектроскопического методов было исследовано строение аценафтилена, а также его олигомерных продуктов, образующихся при иницировании йодом в твердой фазе. Аценафтилен кристаллизуется в ромбической форме в пространственной группе Рва 2. Были определены размеры ячеек, а также вероятные расположения молекул в кристаллической решетке. В олигомерных молекулах с трео-диизотактической конфигурацией мономерные звенья располагаются по ходу винтовой линии, обладающей двухкратной ползущей осью. Были установлены приблизительные размеры кристаллических звеньев в олигомерных цепях. Сравнение строения мономера и олигомерных цепей. Сравнение строения мономера и олигомера указывает на то, что олигомеризация может протекать и за счет сравнительно небольших смещений молекул аценафтилена, т. о., кристалличс ская фаза контролирует процесс, т. е. реакция является топотактической. Это находится в согласии с линейным кинетическим характером процесса полимеризации, описанном в предыдущем сообщении.


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# MEASUREMENT OF SMALL SURFACES BY A CARRIER-GAS ADSORPTION METHOD

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A carrier gas apparatus for adsorption measurements is described which has several advantages over the techniques used to date. The gas flow system has been modified so that the basic composition of the gas mixture passing through the detector remains unchanged when gas mixtures of various composition are passed through the adsorbent holder. The error arising from the non-linearity of the detector has been eliminated. Analysing the relationship between the adsorption (or desorption) rate and the recorded peak area, it has been established that there is no unambiguous correlation between the area and the amount of desorbed nitrogen. This correlation is affected by the time dependence of the concentration peak. The upper limit of the relative error has been estimated as a function of the sample size.

# 1. Introduction

The surface area of solids, especially adsorbents, catalyst supports and catalysts of porous structure is usually measured by the so-called BET method [1]. The isotherm equation derived by BRUNAUER, EMMETT and TELLER allows the calculation of the surface area from adsorption data. For surfaces, which are homogeneous from the aspect of adsorption, the theory based upon multilayer adsorption leads to the following isotherm equation:

$$\frac{1}{\chi^{\sigma}} \frac{x}{1-x} = \frac{1}{\chi^{\sigma}_m c} + \frac{c-1}{c\chi^{\sigma}_m} x \tag{1}$$

where  $x = p/p_0$  is the relative partial pressure of the adsorbed substance in the gas phase;

p = partial pressure of the adsorbed substance;

 $p_0$  = vapor pressure of the adsorbed substance;

 $\chi^{\sigma}$  = the specific, adsorbed excess amount =  $n^{\sigma}/m$ 

 $\chi_m^{\sigma}$  = the specific, adsorbed excess amount corresponding to the monomolecular layer;

m = mass of the adsorbent;

1

c = a constant parameter depending on the heat of adsorption and the temperature.

Plotting the left-hand side of Eq. (1) against x, a straight line is obtained. The values of c and  $\chi_m^{\sigma}$  can be calculated from the slope and the intercept

of this line. If the average surface requirement for one molecule of the adsorbed substance is known, the surface area can be determined from  $\chi_m^{\sigma}$ . In the case of nitrogen this surface requirement is equal to:

 $16.2 \times 10^{-16} \text{ cm}^2/\text{molecule} = 4.37 \text{ m}^2/\text{n} \text{ cm}^3$ 

The range of validity of the BET equation is:

At values higher than x = 0.35 the adsorbed amount is less than expected, owing to the decrease of the adsorption heat when the coverage becomes significant [2].

There are several ways for measuring the adsorbed amount. Besides the traditional, static methods (volumetric, gravimetric) the carrier-gas methods have found widespread use in the last decade.

In the carrier-gas method the gas which undergoes adsorption (e.g. nitrogen) is mixed with a gas (hydrogen or helium) whose adsorption is negligible compared with that of nitrogen at its boiling point. By adjusting the flow velocity appropriately, a gas mixture is obtained, in which the value of x for nitrogen is constant and lies between 0.05 and 0.35. This mixture is passed first over the adsorbent studied and then a hot wire detector, under steadystate conditions. If the adsorbent is immersed into a liquid nitrogen bath, it adsorbs nitrogen from the gas stream. The gas mixture leaving the adsorbent holder will temporarily be of lower nitrogen content. The change of concentration is sensed by the detector and a negative peak will be recorded. If now the adsorbent holder is placed into a room temperature bath, the adsorbed nitrogen will be completely desorbed, and a positive nitrogen concentration peak will appear on the recording. By comparing the peak with that due to a known quantity of nitrogen, the adsorbed amount can be calculated. On repetition of this procedure using carrier gases with different nitrogen-hydrogen ratios, the adsorption isotherm and, consequently, the specific surface can be determined. This method was first used by NELSEN and EGGERTSTEN [7], later by ETTRE et al. [6] and others [3,4,5].

The method outlined below differs in several aspects from the one described above. A more convenient gas mixture is applied, providing for fixation of the working point and the exclusion of the effect of velocity peaks. A linear detector with respect to the composition is applied. The detector is described elsewhere. It will be shown that the recorded signal is generally not proportional to the rate of desorption and the relationship between the peak area and the amount of desorbed nitrogen is not unequivocal even under ideal conditions.

Adsorption studies, in which the apparatus based upon the above principle is used, are under way [9].

### 2. Experimental

# 2.1. Gas system of the apparatus

A significant difference from the principles applied so far is that both gases (nitrogen and hydrogen) are fed into the system at constant rate. The nitrogen flow is then split into two parts. One part (N') adjustable by a needle valve, is mixed with hydrogen: this is the main line. The gas flow of the main line is passed over the adsorbent. The other part, the by-pass line (N'') is combined with the gas mixture leaving the adsorbent holder and is led to the hot wire detector.

The scheme of the apparatus is shown in Fig. 1.



Fig. 1. F — flow stabilizer, M — flowmeter, V – needle valve, B — catalytic burning chamber for the removal of oxygen traces, D — dryer, S — sample holder, I — injector, R — delaying volume, D — detector

Regardless of the ratio set in the main line, both the overall velocity (N + H) and the composition of the mixture passing through the detector remain constant provided that there are no sorption effects. The advantages of this set-up are as follows:

a) Integration can be performed with respect to time only. However the amount of desorbed nitrogen is determined by integration with respect to volume. Thus care must be taken to ensure that the overall velocity of the gas should remain constant and have always the same value in the detector during the registration of the concentration peak. The first requirement is met by separating the concentration and velocity peaks, whereas the second by feed-back of the by-pass line. Thus, unlike in the case described by NELSEN and EGGERTSEN [7], the flow velocity can be taken into account always by the same factor. b) Since the composition of the gas mixture passing through the detector is constant in the reference state, the concentration peak will be superimposed on a uniform concentration base level. Even if the detector is linear in the entire concentration range, *i.e.* its sensitivity is independent of the measured composition, the constant base level is advantageous, since there is no necessity to balance the bridge before each measurement.

# 2.2. The adsorbent

Depending on the type of sample, the adsorbent was prepared by heating for 1-4 hrs at 100-400 °C in a slow, dry gas stream.

During the measurements the formation of large void spaces in the adsorbent holder must be avoided since during heating or cooling, large, undesirable pressure pulses arise from these spaces, partly owing to the thermodiffusion effect. For sample size exceeding 4—5 g the heat transfer becomes too slow and the sorption effect may become drawn out. The expedient amount of adsorbent depends on its specific surface. The sample can be easily measured, if its surface is in the range of 5—20 m<sup>2</sup>.

# 2.3. Detection

The concentration peak was observed by a hot wire detector.

The detector consisted of a copper block with bores in which were placed the sensing elements, made of platinum spiral with a diameter of 1  $\mu$ m and resistivity of 1  $\Omega$ /cm.

The most important problem is to achieve linearity of the detector with respect to the mole fraction. The hot wire detectors are generally linear only in a narrow concentration range. The greater the recorded change of concentration, the larger error is caused by the limited linearity of the detectors. The deviation from linearity can be taken into account by very complex methods only. Therefore, a new type of hot wire detector has been developed which is linear with respect to the mole fraction in the entire concentration range (0-100%) of the nitrogen-hydrogen mixture. Such a detector allows the direct integration of the peak.

# 3. Results and discussion

### 3.1. Transient effects due to the adsorption-desorption processes

Desorption is chosen for the discussion noting that the reverse is true for adsorption. Upon heating the adsorbent holder, the flow velocity and the composition of the leaving gas will change. The change of the velocity is due to two factors:

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a) the gas in the void space of the vessel is expanded;

b) the desorbed nitrogen increases the flow velocity.

Local concentration changes are caused by desorption only. The original flow velocity is restored only after the desorption has been completed. This process may take 1-2 minutes. The peak of the flow velocity appears practically at the same time along the gas line, *i.e.* at the inlet of the by-pass line and in the detector as well.

# Velocity peak

Though the detector is insensitive to the flow velocity in the usual velocity range (10-100 cm<sup>3</sup>/min), a fast velocity peak may cause a small signal which, however does not interfere with the measurement.

# Velocity-concentration peaks

At the junction of the main and by-pass lines the velocity peak forms a concentration peak as well. In the case of desorption when the velocity in the main line increases temporarily, while that in the by-pass line remains constant, the mole fraction of nitrogen is temporarily lowered. The direction of the velocity-concentration peak is generally opposite to the concentration peak of adsorption or desorption. The former would interfere with the measurement only if it were not separated from the concentration peak of adsorption. If there is no by-pass line, or it is not fed back, there will be no velocity-concentration peak. However, the separation of the velocity peak and the concentration peak due to desorption is necessary even in this case. The latter should appear at the detector only after the original velocity has been restored. The velocity-concentration peak allows to check this separation, so in this respect it is advantageous. However, the velocityconcentration peak is due not only to desorption but also to the expansion of the heated gas, therefore, it cannot be applied for the following the desorption.

# Thermodiffusion peaks

If the free volume of the adsorbent vessel is large, a concentration peak caused by the thermodiffusion effect will appear during the heating or cooling. This effect may interfere with the study of very small surfaces with highsensitivity detectors. The effect can be decreased by applying adsorption holders with narrow stocks and filling them up completely with the adsorbent [8].

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# The concentration peak desorption

This peak is the basis of the measurement. By appropriate delaying, it can completely be separated from the velocity and velocity-concentration peaks. The retardation can be realized by inserting a tube of suitable length after the adsorbent holder. It takes several minutes for the concentration peak to pass this tube. Consequently, by the time the concentration peak appears at the inlet of the by-pass line, desorption has been completed and the original flow velocity restored. For example, at a flow velocity of 50 cm<sup>3</sup>/min, 50 cm<sup>3</sup> of tube volume is required for each minute of delay. (In practice this value is somewhat larger owing to the increase of the flow velocity.)

# 3.2. Relationship between the integral of the concentration peak and the volume of desorbed nitrogen

Assuming that the void space in the adsorbent bed is small and the composition is not affected by the expansion, the following equations can be written:

N' IN

$$y' = \frac{\mathbf{N}'}{\mathbf{N}' + \mathbf{H}},\tag{2}$$

(3)

where:

$$y^* = rac{\mathbf{N} + \mathbf{N}_d}{\mathbf{N}' + \mathbf{N}_d + \mathbf{H}},$$

H — feed velocity of hydrogen (cm<sup>3</sup>/min),

- N feed velocity of nitrogen (cm<sup>3</sup>/min),
- N' velocity of nitrogen in the main line (cm<sup>3</sup>/min),
- $N_d$  rate of desorption of nitrogen (cm<sup>3</sup>/min),

y' — mole fraction of nitrogen in the main line before the adsorbent,

- $y^*$  mole fraction of nitrogen in the main line after the adsorbent,
- y mole fraction of nitrogen in the detector,
- $y_0$  mole fraction of nitrogen in the detector at the base level.

If a delaying volume is inserted before the detector, the gas mixture with mole fraction  $y^*$  will arrive at the inlet of the by-pass line at the original velocity equal to N' + H<sup>\*</sup>.

\* It should be noted that if the by-pass line were not fed back, the detector would measure this mole fraction  $(y^*)$ . Then the recorded signal would be equal to  $y^* - y'$ , which is related to the rate of desorption,  $N_d$ , by the following equation:

$$N_d = (H + N') \frac{y^* - y'}{1 - y^*}.$$
 (4)

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The relationship between the integrated signal and the volume of desorbed nitrogen will now be discussed. The volume of desorbed nitrogen

$$V = \int_{-\infty}^{\infty} \mathbf{N}_d \, dt \tag{5}$$

is not equal to the volume measured by the detector. This latter is obtained by taking into account the fact that the detector signal is a linear function of the mole fraction, i.e.

$$V_r = \int_{-\infty}^{\infty} (\mathbf{H} + \mathbf{N}) \, \Delta y \, dt, \tag{6}$$

where

$$\Delta y = y - y_0 \tag{7a}$$

and

$$y_0 \equiv \frac{N}{N+H} . \tag{7b}$$

 $\Delta y$  is the change of mole fraction measured by the detector through the peak.

Our objective is to determine the relationship between V and  $V_r$ . The velocity of nitrogen in the detector (in the presence of a delaying volume) is

$$(N' + H) y^* + N'',$$
 (8)

where N" is the velocity of nitrogen in the by-pass line  $(cm^3/min)$ .

Hence the mole fraction of nitrogen in the detector:

$$y = y^* \frac{N' + H}{N + H} + \frac{N''}{N + H}$$
 (9)

Using Eqs (3), (7) and (9), one obtains

$$\Delta y = y - y_0 = \frac{N_d H}{(N+H) (N'+N_d+H)} .$$
(10)

Substitution of Eq. (10) into (6) yields

$$V_r = \int \frac{\mathbf{N}_d \mathbf{H}}{\mathbf{N}' + \mathbf{H} + \mathbf{N}_d} dt.$$
(11)

From Eq. (11) it is clear that there is generally no simple relationship between the volume of desorbed nitrogen given by Eq. (5) and the recorded integral  $V_r$ .

The following expression is valid

$$V_r = (\mathbf{H} + \mathbf{N}) \int_{-\infty}^{\infty} \Delta y \, dt = (\mathbf{H} + \mathbf{N}') \int_{-\infty}^{\infty} \Delta y^* dt \,, \tag{12}$$

where

$$\Delta y^* = y^* - y' = \frac{HN_d}{(H+N')(H+N'+N_d)}$$
(13)

is the change of mole fraction before the inlet of the by-pass line, as can be calculated from Eqs (2) and (3).

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It was not mentioned so far that the shape of the concentration peak advancing with the gas flow is changed even after the completion of the pressure peak as a result of dispersion effects (diffusion, back-mixing, etc.). However, it can be established that these effects do not alter the volume integral of the concentration peak, *i.e.* 

$$\int_{-\infty}^{+\infty} \Delta y \ dt \ (\text{at the detector}) = \int_{-\infty}^{+\infty} \Delta y \ dt \ (\text{after the inlet})$$

$$\int_{-\infty}^{+\infty} \Delta y^* dt \ (\text{before the inlet}) = \int_{-\infty}^{+\infty} \Delta y^* \ dt \ (\text{after the adsorbent holder}). \tag{14}$$

The dependence of the recorded volume  $V_r$  on the rate of desorption,  $N_d$ , is given invariably by Eq. (11).

Let

and

$$N_d \ll \mathbf{H} + \mathbf{N}' \tag{15}$$

$$V'_r \equiv \int_{-\infty}^{\infty} \frac{\mathrm{HN}_d}{\mathrm{H} + \mathrm{N}'} \, dt \,. \tag{16}$$

Then, using Eqs (5) and (11), we obtain as an approximation

$$V_r \approx V \frac{\mathrm{H}}{\mathrm{H} + \mathrm{N}'} = V_r' \,. \tag{17}$$

In other words, the two volumes (V and  $V_r$ ) are proportional to each other but the proportionality factor varies with the value of the N'/H ratio. If  $V_r$  is replaced by its first approximation viz.,  $V'_r$  defined by Eq. (16), the error of the method will still be determined by the time dependence of  $N_d$ , or more precisely, by the approximation given in Eq. (15) and the error is not decreased by the diffusion of the concentration peak. In estimating the error, the decrease of the relative magnitude of  $y - y_0$  due to diffusion is of no significance. Consequently, in practice either the gas composition should be taken into account by calculation or a calibration is necessary for every composition.\*

\* If  $N_d$  were negligible, *i.e.* the velocity were not increased temporarily by desorption, the volume of desorbed nitrogen could exactly be calculated from the integrated detector signal.

The true volume, however, would be given by

$$V^* = \int_{-\infty}^{\infty} \Delta y^* \left( N' + H + N_d \right) dt \quad (= V'_r)$$
(18)

f the detector were placed immediately at the site of desorption. The detector signal would then be recorded in the following form:

$$V_r^* = \int_{-\infty}^{\infty} \Delta y^* C \, \mathrm{dt} \qquad C = \mathrm{const.}$$
<sup>(19)</sup>

This result is naturally erroneous since the scale of the time axis of the recording is not uniform, and a Stiltjes integral should have been applied.

If the velocity peak has already passed by the time the desorbed nitrogen reaches the detector, the flow velocity will be uniform and equal to N + H, but the recorded value  $V_r$  (see Eq. (12)) will not be given by Eq. (18).

Considering the other extreme case, i.e. when

$$\mathbf{N}_d \gg \mathbf{H} + \mathbf{N}' \tag{20}$$

the following equation can be written

$$\Delta y^* \approx \frac{\mathrm{H}}{\mathrm{H} + \mathrm{N}'} T(t) \quad \text{and} \quad \Delta y \approx \frac{\mathrm{H}}{\mathrm{H} + \mathrm{N}} T(t),$$
 (21)

where T(t) = 1 during the peak, but otherwise T(t) = 0.

Thus, from Eqs (13) and (21), if the peak lasts for  $\Delta t$ , one obtains

$$V_r = \mathbf{H} \, \varDelta \, t. \tag{22}$$

V can be calculated by assuming that the desorbed nitrogen dilutes the gas mixture flowing in the tube and the volume of the desorbed gas past the pressure wave is given by

$$V = (\mathbf{H} + \mathbf{N}') \, \varDelta t \; . \tag{23}$$

Using Eqs (22) and (23) we have

$$V_r = V(1-y').$$
 (24)

Let us examine the error caused by approximation (15). The relative error is

$$\frac{V'_{r}-V_{r}}{V'_{r}} = \frac{\int_{-\infty}^{\infty} \left( \mathbf{N}_{d} \frac{\mathbf{H}}{\mathbf{H}+\mathbf{N}'} - \mathbf{N}_{d} \frac{\mathbf{H}}{\mathbf{H}+\mathbf{N}'+\mathbf{N}_{d}} \right) dt}{\frac{\mathbf{H}}{\mathbf{H}+\mathbf{N}'} V} \leq \frac{1}{\mathbf{H}+\mathbf{N}'} \int_{-\infty}^{\infty} \mathbf{N}_{d}^{2} dt} \cdot \frac{1}{\int_{-\infty}^{\infty} \mathbf{N}_{d} dt} \cdot \frac{\int_{-\infty}^{\infty} \mathbf{N}_{d} dt}{\int_{-\infty}^{\infty} \mathbf{N}_{d} dt} \cdot \frac{1}{\mathbf{H}+\mathbf{N}'} \int_{-\infty}^{\infty} \mathbf{N}_{d} dt} \cdot \frac{1}{\mathbf{H}+\mathbf{N}'} \left( \int_{-\infty}^{\infty} \mathbf{N}_{d} dt \right) \cdot \frac{1}{\mathbf{H}+\mathbf{N}'} \cdot \frac{1}{\mathbf{H}+\mathbf{N}'} \left( \int_{-\infty}^{\infty} \mathbf{N}_{d} dt \right) \cdot \frac{1}{\mathbf{H}+\mathbf{N}'} \cdot \frac{1}{\mathbf{H}+\mathbf{N}'}$$

No constraint can be given for this integral in the general case, but if  $N_d \leq N_{d \max}$  holds true for every moment, then:

$$\frac{V_r'-V_r}{V_r'} \le \frac{N_{d,\max}^2 \int\limits_{-\infty}^{\infty} \frac{N_d^2}{K^2} dt}{(\mathbf{H}+\mathbf{N}')V} \le \frac{N_{d,\max} \int\limits_{-\infty}^{\infty} N_d dt}{(\mathbf{H}+\mathbf{N}')V} = \frac{N_{d,\max}}{\mathbf{H}+\mathbf{N}'} .$$
(26)

The error will be smaller if the flow velocity of the gas mixture is higher or the maximum of the volume flow velocity of the desorbed gas — *i.e.* the peak of the desorption curve — is lower.

Thus, if  $H = 30 \text{ cm}^3/\text{min}$ ,  $N' = 10 \text{ cm}^3/\text{min}$  and  $N_{d, \max} = 1 \text{ cm}^3/\text{min}$ , the upper limit of the relative error is equal to 2.5%, while if  $N_{d, \max} = 5 \text{ cm}^3/\text{min}$ , this limit is equal to 10%.

However, if the considerations are restricted to desorption functions of the type:

$$\mathbf{N}_d = A e^{-a^2 t^2} \tag{27}$$

which correspond to the form of real desorption curves, the volume of desorbed gas can be expressed ad follows:

$$V'_{r} = \frac{\mathrm{H}}{\mathrm{H} + \mathrm{N}'} \int_{-\infty}^{\infty} A e^{-a^{2}t^{2}} dt = \frac{\mathrm{H}A \,\sqrt{\pi}}{(\mathrm{H} + \mathrm{N}') \,a} \,. \tag{28}$$

Using Eqs (20) and (12) the relative error becomes

$$\frac{V'_r - V_r}{V'_r} = \frac{A}{(H+N')\sqrt{2}} = \frac{V_a}{(H+N')\sqrt{2\pi}} .$$
(29)

Let us consider the result of an actual measurement:  $a = 2 \min^{-1}$ ,  $V = 1 \text{ cm}^3$ ,  $H = 30 \text{ cm}^3/\text{min}$ ,  $N' = 10 \text{ cm}^3/\text{min}$ . With these values relative error is equal to 2%. If the volume of desorbed nitrogen is taken as  $V = 5 \text{ cm}^3$ , the relative error under similar flow conditions will be 10%.

# 3.3. Calibration

The problems outlined above are of lesser significance if the nitrogen volume V is determined by the following method. At a point located after the adsorbent holder nitrogen samples of known volume are injected into the gas flow. The known and measured volumes of nitrogen are compared directly. This method was applied by NELSEN and EGGERTSEN [7], and ETTRE and co-workers [6].

Since the injection of the calibrating gas is a process similar to desorption, it is convenient to use the desorption peak for evaluation, as done by the above authors. The possible problems described above can be avoided if the difference between the integrated adsorption and desorption peaks is less than the error limit. (For this condition, the linearity of the detector in the given range is a necessary requirement.) The main source of the experimental errors is the instability of the gas flow, therefore, special attention has been paid to its adjustment and stabilization.

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# THE EFFECT OF THE CELL RESISTANCE IN HIGHER HARMONIC A.C. POLAROGRAPHY IN THE CASE OF DIFFUSION POLARIZATION

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The authors experimentally controlled the relations on the fundamental, second and third harmonic A.C. components, respectively, of the current flowing through an electrode polarized by an A. C. voltage superimposed on the D. C. polarizing potential. These expressions take into account the effect of the cell resistance and refer to diffusion polarization. The experimental results relating to the Fe(III)/Fe(II) and Pb(II)/Pb(Hg) systems were in good agreement with the theoretical data, however, a deviation exceeding the experimental error was found in the case of Tl(I)/Tl(Hg) and Cd(II)/Cd(Hg). In the former system the deviation occurring at more negative potentials than the half-wave potential can be accounted for the specific adsorption of thallium(I) ions while in the latter system the variation of the double layer capacity and the effect of spherical diffusion motivates the results.

Both the A.C. polarographic experiments and the investigations of the electrode processes on an electrode polarized by an A.C. voltage superimposed on the D.C. potential consist in the measurement of the faradaic impedance or the current passing through the latter. However, the experimentally measurable quantity is the cell impedance or the current of the cell and the phase angle. The cell impedance — as a first approximation — can be represented by the equivalent circuit shown in Fig. 1/a consisting of the parallel resultant of the faradaic impedance  $(Z_F)$  and the capacity of the electric double layer (C) viz. the electrode impedance  $(Z_e)$  connected in series with the ohmic resistance  $R_0$ . The latter term comprises the resistance of the solution and of the electrode as well as the inner resistance of the meter employed for the measure-



Fig. 1. Equivalent circuit of the cell

ment. The ohmic potential arising on  $R_0$  considerably affects the experimental data. This error can be reduced by employing a potentiostatic measuring technique [1], however, the ohmic drop appearing on the solution layer between the working electrode and the tip of the capillary of the reference electrode cannot be compensated by a potentiostat. In previous communications [2,3] formulas have been derived for the correction of the potentiostatically uncompensated cell resistance in the investigation of the fundamental and second harmonic [2] as well as in that of the third harmonic component [3], respectively, of the A.C. current passing through an electrode polarized by a small amplitude sinusoidal A.C. voltage superimposed on the D.C potential in the case of diffusion polarization. Thus the formulas relating to the harmonic components of the A.C. current were derived in a general form [4,5]. In the A.C. polarographic experiments reported in the literature (cf. e.g. [6]) the effect of the ohmic potential drop was either neglected (the latter procedure is justified when the uncompensated cell resistance is very low, say a few ohms) or it was approximately taken into consideration only [2].

In order to obtain the accurate correction term for the higher harmonic A.C. components under potentiostatic experimental conditions, the equivalent circuit of the cell has been modified according to Fig. 1/b. The higher harmonic components of the A.C. current are generated in the cell because of the nonlinearity of the faradaic impedance as an undistorted sinusoidal voltage viz. not containing higher harmonics - is imposed on the electrode. The capacity of the double layer is supposed to be independent of the potential in the potential range used in the experiments. Thus the electrode impedance can be represented by a current generator having an inner resistance equal to  $Z_{e}(n \omega)$ . Moreover points A and B of the cell can be represented in short circuit because they are at the same potential as referred to higher harmonics. The expressions relating to the fundamental, second and third harmonic components, respectively, of the A.C. current have been derived on the basis of the modified equivalent circuit taking into account the voltage divider formed by the electrode impedance  $(Z_e)$  and the cell resistance  $(R_0)$  (Fig. 1/a). The uncompensated ohmic potential drop appearing on the cell resistance is accurately given by these expressions. Thus we obtain the fundamental harmonic A.C. current density as a function of the overpotential

$$i_{1} = \eta_{\sim}^{0} \frac{\left| \sqrt{\left(\frac{1}{R_{p}}\right)^{2} + \left(\frac{1}{R_{p}} + \omega C\right)^{2}}}{\left| \sqrt{\left(1 + \frac{R_{0}}{R_{p}}\right)^{2} + \left(\frac{R_{0}}{R_{p}} + \omega R_{0}C\right)^{2}}}\right|, \qquad (1)$$

while the amplitudes of the second and the third harmonic A.C. current density, respectively, are the following:

$$\begin{split} |i_{2}| &= \frac{(zF)^{3}}{2\sqrt{2}(RT)^{2}} \sqrt[7]{\omega} (C_{10}\sqrt{D_{1}} + C_{20}\sqrt{D_{2}}) \frac{e^{zF/RT(\eta_{-}-\eta_{1/2})} |1 - e^{zF/RT(\eta_{-}-\eta_{1/2})}|}{(1 + e^{zF/RT(\eta_{-}-\eta_{1/2})})^{3}} \cdot \\ &\cdot \frac{\eta_{\sim}^{02}}{\left[ \left[ 1 + \frac{R_{0}}{R_{p}(\omega)} \right]^{2} + \left[ \frac{R_{0}}{R_{p}(\omega)} + \omega R_{0}C \right]^{2} \right] \cdot \sqrt[7]{\left[ 1 + \frac{R_{0}}{R_{p}(2\omega)} \right]^{2} + \left[ \frac{R_{0}}{R_{p}(2\omega)} + 2\omega R_{0}C \right]^{2}}} \\ |i_{3}| &= \frac{\sqrt{3}}{192} \frac{(zF)^{4}}{(RT)^{3}} \sqrt[7]{\omega} (C_{10}\sqrt{D_{1}} + C_{20}\sqrt{D_{2}}) \frac{\left| 3 - 2ch^{2}\frac{zF}{2RT}(\eta_{-}-\eta_{1/2}) \right|}{ch^{4}\frac{zF}{2RT}(\eta_{-}-\eta_{1/2})} \cdot \\ &\cdot \frac{\eta_{\sim}^{03}}{\left[ \left[ \left( 1 + \frac{R_{0}}{R_{p}(\omega)} \right)^{2} + \left[ \frac{R_{0}}{R_{p}(\omega)} + \omega R_{0}C \right]^{2} \right]^{3/2} \right] \sqrt{\left[ \left( 1 + \frac{R_{0}}{R_{p}(3\omega)} \right)^{2} + \left[ \frac{R_{0}}{R_{p}(3\omega)} + 3\omega R_{0}C \right]^{2}} \right]} \end{split}$$

where

 $C_{10}$  is the bulk concentration of the reduced form of the component of the electrode reaction

 $C_{20}$  is the bulk concentration of the oxidized form of the component of the electrode reaction

C is the capacity of the electric double layer

 $D_1$  is the diffusion coefficient of the reduced form of the electroactive species

 $D_2$  is the diffusion coefficient of the oxidized form of the electroactive species

- F is the Faraday constant
- R is the universal gas constant
- $R_0$  is the uncompensated cell resistance
- T is the absolute temperature
- z is the number of electrons involved in the electrode reaction
- $\eta_{\pm}$  is the time average value of the overpotential
- $\eta_{1/2}$  is the half-wave potential

 $\eta^0_{\sim}$  is the amplitude of the A.C. voltage imposed on the cell impedance  $\omega$  is the angular frequency of the A.C. voltage and

 $R_{\rm p}(n\,\omega)$  is the polarization resistance taking into account that the Faraday

impedance  $(Z_F(n \omega))$  is the parallel resultant of the polarization resistance and the pseudo-capacity  $(C_P(n \omega))$ 

$$\frac{1}{Z_F(n\omega)} = \frac{1}{R_p(n\omega)} + jn\omega C_p(n\omega)$$
(4)

and

$$\frac{1}{R_{p}(n\omega)} = n\omega C_{p}(n\omega) = \frac{(zF)^{2}}{\sqrt{2} RT} \sqrt{n\omega} (C_{10}\sqrt{D_{1}} + C_{20}\sqrt{D_{2}}) \frac{e^{zF/RT} (\eta_{*} - \eta_{1/2})}{(1 + e^{zF/RT} (\eta_{*} - \eta_{1/2}))^{2}}$$
(5)

in the case of diffusion polarization (n = 1, 2 or 3 in the expressions relating) to the fundamental, second or third harmonics, respectively).

Measurements were made by employing a dropping mercury electrode in order to check experimentally the validity of the above formulas.

The electrode reactions of the systems selected for this investigation had to be controlled by diffusion. This condition is practically fulfilled when the heterogeneous rate constant of the transition reaction — according to the calculations referring to transition and diffusion polarization (4 through 7) is  $k > 1 \text{ cms}^{-1}$  since in this case, the functions of the harmonic components of the A.C. current vs. potential are equal within the experimental error to the ones calculated for diffusion polarization in the frequency range  $\omega <$  $< 2000 \ s^{-1}$ .

Several authors have investigated the reaction of iron(III), lead(II), thallium(I) and cadmium(II) on the dropping mercury electrode in various supporting electrolytes. According to the results of independent measurements the following systems comply with the above mentioned condition: Fe(III)/Fe(II) in 0.5  $M K_2(COO)_2$ ; Pb(II)/Pb(Hg) in 1  $M HClO_4$ ; Tl(I)/Tl(Hg) in 1  $M KNO_3$  and Cd(II)/Cd(Hg) in 1 M HCl. The heterogeneous rate constants of the above transition reactions at their respective equilibrium potentials on the d.m.e. are listed in Table I.

System	Supporting electrolyte	$k \text{ cms}^{-1}$	References
Fe(III)/Fe(II)	0.5 M K <sub>2</sub> (COO) <sub>2</sub>	>1	(Ref. [16])
	1 M HClO <sub>4</sub>	2.0	(Ref. [16])
Pb(II)/Pb(Hg)	1 M NaClO <sub>4</sub>		RANDLES, J. E. B.: Trans. of the Symp. on
	(pH = 2)	3.3	Electrode Processes, New York 1959.
	1 M KNO <sub>3</sub>	>1	Ed. Jeager, E. J. Wiley, New York,
	1 M KNO <sub>3</sub>	0.8	1961
Cd(II)/Cd(Hg)	1 M KCl	2.9	BARKER, C. G., FAIRCLOTH, R. L.,
	1 M KCl	1.2	GARDNER, A. W.: Nature 181, 247 (1958)
	1 M KCl	$\sim 5$	FRISCHMANN, J. K., TIMNICK, A.: Anal.
	1 M HCl	0.6	Chem. 39, 507 (1967)
	1 M HCl	0.94	
Tl(I)/Tl(Hg)	1 M KNO <sub>3</sub>	>1	(Ref. [16])
	1 M NaClO <sub>4</sub>	>1	BARKER, G. C., FAIRCLOTH, R. L.,
	$0.5 M \operatorname{Na_2SO_4}$	3.1	GARDNER, A. W.: Nature 181, 247 (1958)

 Table I

 Heterogeneous rate constants of the transition reactions

The equivalent conductance of the supporting electrolytes ranges from 70 to 350  $Ohm^{-1}$  cm<sup>2</sup> [8]. Thus Eqs (1), (2) and (3) could be examined in a relatively wide range of cell resistance encountered in practical polarography.

The experimental method for the verification of Eqs (1), (2) and (3) consisted in the potentiostatic measurement of the harmonic components of the A.C. current as a function of the potential in the entire range of the polarographic wave of the respective systems. The measured data were compared to the ones calculated by means of the above formulas.

In the calculations we employed the experimentally controlled parameters and the individual constants of each system (D, z) as well as the double layer capacity and cell resistance data determined in separate experiments in each case.

### **Experimental part**

The block diagram of the potentiostatic measuring system is represented in Fig. 2. The D.C. voltage was adjusted on potentiostat (1). The A.C. voltage superimposed on the D.C. potential by means of the potentiostat was supplied by low-distortion sine wave generator (2). The distortion of the latter was lower than 0.1 per cent at the output voltage used in the measurements. The polarization potential and the amplitude of the superimposed A. C. voltage was measured against a normal calomel electrode (3). The measurement of the potential was performed by D.C. voltmeter (4) having a 10<sup>12</sup> ohm input impedance while the amplitude of the A. C. voltage was measured by 1 Mohm input impedance A. C. voltmeter (5). The harmonic components of the A.C. current flowing through the cell were determined at the appropriate frequency by the measurement of the voltage drop across a 100 or 1000 Ohm standard resistor (6) connected in series with the anode. Audio-frequency wave analyzer (7) served for the selective measurements. The sensitivity of the latter was 1  $\mu$ V. Thus the maximum current sensitivity of the equipment was  $10^{-9}$  A.

A three-electrode polarographic cell was employed in the experiments. The tip of the Luggin capillary of the calomel electrode was placed 1 to 3 mm near to the d.m.e. The calomel electrode served for the measurement and the control of the polarization potential and the amplitude of the A. C. voltage. A mercury pool electrode was used as an anode. The dropping time of the d.m.e. was adjusted to 4s approximately.

The potential was varied in steps of 5 or 10 mV, while the amplitude of the A. C. voltage was maintained at a constant value of  $10 \text{ mV}_{eff}$ .



Fig. 2. Block diagram of the experimental equipment

The solutions were prepared from analytical grade reagents and high purity distilled water. Thoroughly purified nitrogen served to deaerate the solutions prior to the measurements. Readings were effected at the maximum current intensity of the mercury drop and the mean of 5 to 10 readings was accepted as a measured data. The deviation of the readings from the mean was generally 2 to 4 per cent. The measurements were performed at  $20 \pm 2$  °C.

# Determination of the capacity of the double layer and of the uncompensated cell resistance

The auxiliary data required for the calculations of the harmonic components of the A.C. current, namely the capacity of the double layer (C) and the uncompensated cell resistance  $(R_0)$  were determined in the supporting electrolyte not containing any depolarizer by means of the above experimental equipment using a cell arrangement and a dropping time of the d.m.e. identical to that used in the measurement of the current-potential curves.

In order to determine the double layer capacity an A.C. voltage having an amplitude of 10  $mV_{eff}$  and a frequency of 64 Hz was superimposed on the d.m.e. and the fundamental harmonic A. C. current was measured as a function of the potential in the voltage range corresponding to the polarographic wave of the respective ion.

In an electrolyte not containing any depolarizer the cell impedance is equal to the series resultant of the  $R_0$  resistance and the double layer capacity C [1]:

$$Z = \sqrt{R_0^2 + \frac{1}{(\omega C)^2}} \tag{6}$$

and the amplitude of the fundamental harmonic A.C. current flowing through the cell is

$$|i_1| = \frac{|\eta_{\infty}^0|}{|Z|}$$
 (7)

It follows that the double layer capacity is given by

$$C = \frac{1}{\omega} \left[ \frac{\eta_{\sim}^{02}}{i_1^2} - R_0^2 \right]^{-1/2}.$$
 (8)

The determination of the cell resistance is based on the fact that at sufficiently high frequency

$$R_0 \gg \frac{1}{\omega C}$$

*i.e.*  $1/\omega C$  is negligible as compared to  $R_0$  and, thus

$$Z = R_0$$
.

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The frequency dependence of the cell impedance was found to be negligible above 3000 Hz in agreement with literature data [9, 10]. Accordingly an A.C. voltage of 5000 Hz frequency and 10 mV amplitude was used for the measurement of the cell resistance at the half-wave potential of the respective ion.  $R_0$  was calculated according to Ohm's law from the amplitude of the A.C. current.

# Determination of the surface area of the electrode

The mean surface area of the electrode was evaluated in the usual manner. 50 drops of mercury were collected at the half-wave potential of the respective ions and the mercury was weighed after rinsing with ether, and drying. The mean surface area of the electrode was determined before and after the experiments by adjusting an equal height of mercury column.

# Results

The data of the cell resistance  $(R_0)$ , the double layer capacity (C) and of the mean surface area of the electrode (q) in the respective supporting electrolyte and at the half-wave potential of the corresponding ions are listed in Table II.

System	Supporting electrolyte	Capacity of double layer µF/cm <sup>2</sup>	Cell resistance Ohm	$\begin{array}{c} \text{Surface area of} \\ \text{the electrode} \\ q \cdot 10^2 \text{ cm}^2 \end{array}$
Fe(III)/Fe(II)	0.5 M K <sub>2</sub> (COO) <sub>2</sub>	50.0	47.2	3.90
Pb(II)/Pb(Hg)	1 M HClO <sub>4</sub>	33.4	67.7	2.82
Cd(II)/Cd(Hg)	1 M HCl	30.5	25.6	4.10
Tl(I)/Tl(Hg)	1 M KNO <sub>3</sub>	33.0	43.0	3.72

Table II

The individual constants characteristic to the electrode processes of the ions under investigation are summarized in Table III.

No unequivocal and generally accepted values were found in the literature for the diffusion coefficients of the electroactive species. (The diffusion coefficients of the oxidized form of the ions were only needed as the solutions contained the latter).

The diffusion constants generally accepted in the course of investigations in the presence of a large quantity of inert electrolyte are those obtained in the measurement of the polarographic diffusion current and evaluated according to the equation of ILKOVIČ or that of KOUTECKY—STACKELBERG [11, 12].

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System		ILKOVIČ's equation		KOUTECKY – STACKELBERG's equation		Impendance measurement		Value accepted in this
System	Z	$D \cdot 10^5 \ { m cm}^{2}{ m s}^{-1}$					work	
			Ref.		Ref.		Ref.	
Fe(III)/Fe(II)	1	0.77	[1]			0.49	[2]	0.44
0.5 $M  \mathrm{K}_2(\mathrm{COO})_2$						0.40	[3]	
Pb(II)/Pb(Hg)	2	1.24	[4]	0.94	[4]	1.04	[4]	0.99
0.5 M NaClO <sub>4</sub>		0.95		18.0				
Cd(II)/Cd(Hg)	2	1.02	[4]	0.78	[4]	0.87	[4]	0.83
1 M HCl						0.89	[5]	
Tl(I)/Tl(Hg)	1	1.9	[1]			2.00	[6]	1.95
1 M KNO <sub>3</sub>						2		

### Table III

Diffusion constants and number of electrons involved in the electrode reaction

[1]	MARTENS, P. H., NANGNIOT, A. P.: Bull. Inst. Agron. et Stat. Rech. Gembloux,
	24, 286 (1956)
[2]	Cf. Ref. [20]
[3]	Cf. Ref. [19]
[4]	Cf. Ref. [13]
[5]	Cf. Ref. [14]
[6]	SLUYTERS-REHBACH, M., TIMMER, B., SLUYTERS, J. H.: Rec. Trav. Chim. Pays-
	Bas. 82, 553, (1963)

However, the data calculated from impedance measurements [13, 14] cannot be left out from consideration when A.C. techniques are employed. Thus the mean of the diffusion coefficients obtained in D.C. and A.C. experiments, respectively, were adopted in the calculations.

The experimentally obtained data and the calculated current potential curves\* are represented in Figs 3 through 10.

The curves relating to the case when  $R_0 = 0$  are denoted by dotted lines while the full lines indicate the curves calculated by using the measured values of the cell resistance and the dots represent the measured data.

Fig. 3 shows the amplitudes of the fundamental  $(I_1)$  and second  $(I_2)$  harmonic A.C. component of the current, respectively, as a function of the

<sup>\*</sup> The calculations were performed on the computer (type ODRA) of the Computer Center of the Veszprém University of Chemical Engineering.

potential in the case of the Fe(III)/Fe(II) system in 0.5 M K<sub>2</sub>(COO)<sub>2</sub>. Figs 5 and 7 represent the fundamental, second and third ( $I_3$ ) harmonic A.C. currents respectively as a function of the potential in the case of Pb(II)/Pb(Hg) in 1 M HClO<sub>4</sub> and Cd(II)/Cd(Hg) in 1 M HCl respectively.

The potential dependence of the second harmonic A.C. current of Tl(I)/Tl(Hg) in 1 M KNO<sub>3</sub> is shown in Fig. 9. The frequency of the A.C. voltage employed in the measurements and the concentration of the solutions is indicated in the figures.

Figs 4, 6, 8 and 10 represent the maximum amplitude of the A.C. harmonics as plotted *vs.* the square root of the frequency of the A.C. voltage in the case of the four systems, respectively.



Fig. 3. (a) fundamental and (b) second harmonic A.C. current as a function of the potential in Fe(III) solutions

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Fig. 4. Maximum intensities of the fundamental harmonic (a) and second harmonic (b) A.C. current as a function of the square root of frequency of A.C. voltage in Fe(III) solutions



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Fig. 6. Maximum intensities of the fundamental harmonic (a) and second harmonic (b) as well as third harmonic (c) A.C. current as a function of the square root of frequency of A.C. voltage in Pb(II) solutions





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Fig. 7. (a) fundamental harmonic, (b) second harmonic and (c) third harmonic A.C. current as a function of the potential in Cd(II) solutions

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b)



Fig. 8. Maximum intensities of the fundamental harmonic (a) and second harmonic (b) as well as third harmonic (c) A.C. current as a function of the square root of frequency of A.C. voltage in Cd(II) solutions

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a)



Fig. 9. Second harmonic A.C. current as a function of the potential in Tl(I) solutions



Fig. 10. Maximum intensities of the second harmonic A.C. current as a function of the square root of frequency of A.C. voltage in Tl(I) solutions

# Discussion

Several authors investigated the relations referring to faradaic impedance either by the determination of the cell impedance [15 through 17] or by measurement of the fundamental harmonic component of the A.C. current appearing on the faradaic impedance [18, 19]. However, meager data were only reported in the literature concerning the second harmonic component of the A.C. current flowing through the electrode polarized by an A.C. voltage superimposed on the D.C. potential [20, 21] while quantitative meas urements of the third harmonic A.C. component have not yet been performed [3].

The experimental data referring to the Fe(III)/Fe(II) system (Figs 3 and 4) agree with the calculated curves within the experimental error. DE-LAHAY and ADAMS [18] have found a considerable deviation between the experimentally obtained data and the ones calculated for the fundamental harmonic A.C. current in course of their earlier investigations, while the results of the measurements of UNDERKOFLER and SHAIN [19] on the hanging mercury drop electrode were in good agreement with the theoretical data. The latter results are supported by the data shown in Figs 3a and 4a.

The experiments referring to the second harmonic A.C. component (Figs 3b and 4b) complement the study of SMITH and REINMUTH [20] performed in a comparatively narrow range of frequencies ( $\nu < 80$  Hz).

The investigations on the Pb(II)/Pb(Hg) system (Figs 5 and 6) also support the validity of the expressions relating to the harmonic component of the A.C. current.

The agreement between the calculated and measured data, respectively, was less satisfactory in the case of Cd(II)/Cd(Hg) (Figs 7 and 8) and Tl(I)/Tl(Hg) (Figs 9 and 10) as the assumptions used in the calculations were not fulfilled in these systems (namely the double layer capacity was not constant, independent from the potential and equal to the capacity value obtained in the supporting electrolyte not containing any depolarizer).

The double layer capacity varies from 24 to 35  $\mu$ F/cm<sup>2</sup> in 1N hydrochloric acid employed as a supporting electrolyte for the study of Cd(II)/Cd(Hg) [22]. The deviation of the fundamental harmonic A.C. current data from the calculated curves at higher frequencies can be attributed to this fact. A discrepancy exceeding the experimental error was also found between the calculated and measured data referring to the second harmonic at more negative potentials than the half-wave potential of cadmium ions, while the agreement was found to be satisfactory between theoretical and experimental values at more positive potentials than the half wave potential. It is noteworthy that the relations obtained by calculations based on the assumption of linear diffusion are inconsistent with those derived on the basis of the spherical

electrode model in the case of amalgam-forming electrode reactions according to SMITH et al. [23]. Namely, the second harmonic A.C. current is predicted to be larger in the case of spherical diffusion than the values calculated according to the planar electrode model. The deviation between the above mentioned expressions is considerable at more negative potentials than the half-wave potential while at more positive potentials than the latter the neglection of spherical diffusion causes a slight error only in the case of reversible amalgam-forming polarographic reactions. According to DELMASTRO and SMITH [24] the difference between the data relating to the planar and to the spherical electrode model, respectively, does not exceed the experimental error in the entire range of the potentials of the polarographic step of reversible polarographic redox reactions. The discrepancy of the measured data and the calculated ones in Figs 7 and 8 is consistent with the considerations concerning the spherical model of the electrode in the case of the Cd(II)/Cd(Hg) system at more negative potentials than the half-wave potential. However, further investigations are required in order to account quantitatively for the above effects and for those of the non-linearity of the electric double layer. The experimental results shown in Fig. 7 can be attributed both to the effect of the non-linearity of the double layer and to that of spherical diffusion.

The double layer capacity was found to be practically independent of the potential in the supporting electrolyte and over the potential range suitable for the study of the Pb(II)/Pb(Hg) system. However, the effect predicted for the case of amalgam-forming reaction was not exhibited on the curves representing the second harmonic A.C. current of Pb(II) solutions as a function of the potential (Fig. 5b) as the experimental data were in fairly good agreement with those calculated on the basis of the planar diffusion in the entire range of potentials. Presumably the effect of spherical diffusion was compensated under the experimental conditions of this study by other factors (depletion, mixing, screening effect of the capillary etc.) [11, 12] influencing the evaluation of the expressions taking into account the effect of spherical diffusion. DELMASTRO and SMITH [24] attributed this fact to the lack of quantitative agreement between the theoretical relations and the results of their measurements of the fundamental harmonic A.C. current in the case of some amalgam-forming reactions.

The double layer capacity is considerably altered by the specific adsorption of thallium ions in Tl(I)/Tl(Hg) system (cf. e.g. [25, 26, 27]). According to SLUYTERS et al. [28] a maximum proportional to the concentration of thallium ions is found on the double layer capacity vs. potential function in the potential range more negative than the half-wave potential of thallium(I). These results are in substantial agreement with the data of Fig. 9 indicating a coincidence of the experimental values and the calculated ones for thallium(I)

at more positive potentials than the half-wave potential while at more negative potentials than the latter a considerable deviation is found.

An inspection of the data referring to the fundamental harmonic A.C. current reveals that the maximum intensity of the latter is not a linear function of the square root of the frequency in the case of the curves calculated for  $R_0 = 0$  (Figs 4a, 5a, and 6a). A similar phenomenon is observed in the case of the curve referring to the Fe(III)/Fe(II) system (Fig. 4a). The harmonic A.C. current is the vectorial resultant of the currents flowing through the double layer capacity and the faradaic impedance, respectively. The faradaic current is proportional to the square root of the frequency while the condenser current varies linearly with the frequency. The amplitude of the capacitive component of the fundamental harmonic proportional to the frequency is relatively larger than the faradaic current when the impedance of the double layer capacity is small as compared to the faradaic impedance by a given cell resistance. However, the amplitude of the fundamental harmonic A.C. current decreases by increasing frequencies under the effect of the ohmic potential drop. Thus a linear relation between the amplitude of the fundamental harmonic and the square root of the frequency is encountered when the two opposite effects compensate each other and a deviation is found from the linear relation depending on the relative magnitude of the cell resistance, the double layer capacity and the faradaic impedance.

The results referring to the second harmonic A.C. current give evidence of the fact that the application of the approximate correction taking into account the voltage drop on the cell resistance instead of the correct expression (given by Eq. (2)) is only satisfactory at low frequencies and at low concentrations. This is illustrated by the pointed curve in Fig. 6b showing the maximum amplitude of the second harmonic A.C. current as a function of the square root of the frequency, a function calculated by taking into account the above mentioned voltage divider while neglecting the factor derived from the shunting effect of the electrode impedance. It is apparent in the figure that the deviation between the latter curve and the experimental values is increasing by increasing frequencies.

The curves relating to the third harmonic A.C. current (Figs 4c, 5c and 6c) reveal that the effect of the cell resistance is increasing in the measurement of higher harmonics. It is apparent that the amplitude of the third harmonic decreases to the largest extent under the effect of the cell resistance in the neighbourhood of the half-wave potential.

The results of this study give experimental evidence of the correctness of Eqs (1), (2) and (3) referring to the harmonic components of the A.C. current flowing through an electrode polarized by an A.C. voltage superimposed on the D.C. potential in the case of diffusion polarization.

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# INFRARED SPECTROPHOTOMETRIC INVESTIGATION OF THE STRUCTURE OF PARATUNGSTATE HYDRATES

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The IR spectra of paratungstate hydrates and of deuterated ammonium paratungstate 5-hydrate have been investigated between 400 and 4000 cm<sup>-1</sup>. It has been found that the frequency, shape and intensity relations of the bands in the region of the W—O vibrations are approximately identical, and the spectra of the microcrystalline salts are, to a very good approximation, independent of the point group symmetry of the crystal. The only difference found in the region of the stretching vibration of the terminal W—O groups is that the band exhibited in the spectra of the 28- and 11-hydrates at 940 cm<sup>-1</sup> is split in the case of the 7-hydrate into 2, and in that of the 5-hydrate into 3 bands. This splitting is attributed to the differences between the bonds of type W—O(I), appearing with decreasing hydrate content. It has been established that paratungstates contain in a smaller quantity also structural OH groups.

tablished that paratungstates contain in a smaller quantity also structural OH groups. Thermocondensation and spectral investigations indicate unequivocally that of the basic structures proposed by LINDQVIST ( $[W_{12}O_{46}]^{20-}$ ) and by LIPSCOMB ( $[W_{12}O_{42}]^{12-}$ ) the latter agrees with the experimental findings, so that the structure  $[W_{12}O_{40}(OH)_2]^{10-}$  proposed for the paratungstate ion can be considered as of general validity.

The investigation of the thermocondensation of ammonium pratungstate 5-hydrate has led to new information and, at the same time, to the recognition of certain problems related to its conversion into  $WO_3$  [1-4]. For a deeper analysis of the reaction steps, the structure of the paratungstate parent compounds should be known, with particular reference to the character of the chemical bonds and crystallographic positions of the lighter groups and radicals linked to the polyanions. Our study of the characteristic vibrational frequencies of paratungstates of different degree of hydration in the range from 400 to 4000 cm<sup>-1</sup> has been undertaken with the aim of obtaining new data on the structure.

### Experimental

### a) Preparation of the hydrates

90 g of tungsten trioxide hydrate (WO<sub>3</sub>  $\cdot$ H<sub>2</sub>O) was suspended in 300 ml of distilled water and dissolved under stirring by the addition of 180 ml 4.2N NH<sub>4</sub>OH. After two hours of standing, the colloidal particles were separated from the solution on a G4 glass filter. The 11-hydrate was precipitated at room temperature, the 7-hydrate between 45 and 50 °C, and the 5-hydrate above 90 °C. Under vigorous stirring, the clear solution was slowly (40-50 min) neutralized with HCl of a density of 1.19 to a pH value of 7.1-7.3. The crystalline precipitate formed was collected on a G3 glass filter, washed with 150-200 ml of 1% NH<sub>4</sub>OH and dried for 3 hrs at room temperature, first under air exhaust, then in vacuum of  $10^{-1}$  mmHg. The 5-hydrate was dried for another hour at 80 °C. According to the X-ray diffraction

and microscopic analysis of the crystal grains, the structural and morphological properties corresponded to those characteristic of 11-, 7- and 5-hydrates [5-6]. Sodium paratungstate. 28-hydrate was prepared by the method of GLEMSER [7]. Table I contains the results of chemical analysis.

Paratungstate	WO <sub>3</sub> %	NH <sub>3</sub> %	H <sub>2</sub> 0 %	Composition
5-hydrate	88.73	5.43	5.84	$5(\mathrm{NH}_4)_2\mathrm{O} \cdot 12\mathrm{WO}_3 \cdot 5\mathrm{H}_2\mathrm{O}$
7-hydrate	87.60	5.34	7.06	$5(NH_4)_2O \cdot 12WO_3 \cdot 7.45H_2O$
11-hydrate	86.0	5.30	8.70	$5(\mathrm{NH_4})_2\mathrm{O}$ · 12WO <sub>3</sub> · 10.6H <sub>2</sub> O

 Table I

 Analytical composition of ammonium paratungstate hydrates

## b) Measuring procedure

Infrered spectra were recorded with a Model UR-10 spectrophotometer in KBr discs, in Nujol and in hexachlorobutadiene. Solid samples containing heavy water were prepared from the finely pulverized substance partly at room temperature, partly at about 80-100 °C in 99.6% D<sub>2</sub>O. At room temperature, the substances were prepared by shaking in D<sub>2</sub>O in a closed system, while in the vicinity of 100 °C they were prepared in the usual way in a distilation system equipped with a P<sub>2</sub>O<sub>5</sub> protection system and a reflux condenser.

## **Experimental** results

According to Figs 1 and 2, with the exception of the  $NH_4$  bands, the spectra of paratungstates show the same characteristics regardless of their degree of hydration. In the region of the terminal  $\nu$ W—O vibrational bands the only difference observed is that the band exhibited in the spectra of the 28-hydrate and the 11-hydrate at 940 cm<sup>-1</sup> is split in the case of the 7-hydrate into two, in the case of the 5-hydrate into three bands. In the region of the  $\nu$ OH bands the development of a fine structure can be observed, which permits the conclusion that hydrogen bonds of various strength are formed.

We have found that at room temperature there is only a slight  $H \rightarrow D$  exchange in the 11- and 7-hydrates even after shaking in  $D_2O$  for several weeks. The  $H \rightarrow D$  exchange is somewhat more pronounced with the 28- and 5-hydrates, however, the spectra of the samples do not seem suitable for a reliable analysis of the deuterated groups. Above 80 °C, there is appreciable deuterium exchange. However, since both the 11- and 7-hydrates are converted at this temperature to the 5-hydrate, the results are actually characteristic of this latter compound. On the other hand, we have found for the deuteration of the 28-hydrate carried out in the temperature range of 70–80 °C that the structure of the crystals separating from the solution after cooling differs substantially from that of the original *para*-crystal, so that the spectral bands associated with deuterium exchange are not characteristic of the initial com-

pound. Therefore, in Figs 1 and 2 only the spectrum of the deuterated 5-hydrate is shown, which is satisfactory in every respect. Spectrum 5 shows that the  $OH \rightarrow OD$  conversion becomes practically complete in the vicinity of 100 °C.



Fig. 1. IR spectra of paratungstate hydrates, 1. Sodium paratungstate  $\cdot$  28 H<sub>2</sub>O; 2. Ammonium paratungstate  $\cdot$  11 H<sub>2</sub>O; 3. Ammonium paratungstate  $\cdot$  7 H<sub>2</sub>O; 4. Ammonium paratungstate  $\cdot$  5 H<sub>2</sub>O; 5. 5-Hydrate deuterated at 100 °C

The regions of the vibrational frequencies of OH and NH groups and of their deuterated forms are known often to overlap, which makes the assignment of the bands difficult. To facilitate orientation, the spectra of anhydrous ammonium chromate  $((NH_4)_2CrO_4)$  and tungsten trioxide hydrate  $(WO_3 \cdot H_2O)$ have been recorded before and after deuteration (Figs 3 and 4). It has been established for the latter that no metal-bonded hydroxo groups are present, so that the compound can be considered as a typical oxyhydrate [8]. Therefore,

the first compound helps in the identification of paratungstate bands corresponding to the vibrations of  $NH_4^+$ ,  $ND_4^+$  and partially deuterated ions, while the latter compound assists the identification of bands arising from the vibrations of  $H_2O$  and  $D_2O$ .

The wavenumbers, assignments and shift ratios of the spectral bands of paratungstate hydrates,  $(NH_4)_2CrO_4$  and  $WO_3 \cdot H_2O$  are summarized in Tables II and III. The frequencies observed in Nujol and hexachlorobutadiene differ only slightly from those in potassium bromide, indicating that there is no substantial interaction between KBr and paratungstates. The interpretation of the data in Tables II and III will be discussed in detail.



Fig. 2. IR spectra of paratungstate hydrates. 1. Sodium paratungstate  $\cdot$  28 H<sub>2</sub>O; 2. Ammonium paratungstate  $\cdot$  11 H<sub>2</sub>O; 3. Ammonium paratungstate  $\cdot$  7 H<sub>2</sub>O; 4a. Ammonium paratungstate  $\cdot$  5 H<sub>2</sub>O (in KBr); 4b. Ammonium paratungstate. 5 H<sub>2</sub>O (in hexachlorobutadiene); 5. 5-Hydrate deuterated at 100 °C

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Fig. 3. IR spectra of (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> and WO<sub>3</sub> ·H<sub>2</sub>O. 1. Ammonium chromate (anhydrous);
 2. Ammonium chromate (deuterated);
 3. Tungstene trioxide hydrate;
 4. Tungstene trioxide hydrate, deuterated

# Discussion

# a) Views on the structure of the paratungstate ion

No uniform picture has yet been formed concerning the complicated structure of paratungstates. This is primarily due to the difficulties connected with the determination of the geometrical position of the oxygen atoms in the vicinity of tungsten and on the other hand to experimental difficulties involved in the simultaneous detection of free and bonded hydroxyl groups and water molecules of crystallization and in the study of their bonding characteristics. Thus, often the formulas of isopoly and heteropoly acids, deduced from various

28-hydrate		11-hy	drate	7-hy	7-hydrate		lrate	Assignment	5-hydrate deuterated	Assignment	Shift ratio
a	b	a	ь	a	b	a	b	-	a b		
404		404		403		405		1	405		
435		438		436		430		δ <b>W</b> —0—W	440		
494		496		498		500			500		
532		528		531		534		Í	534		
-		560		555		555		δOH (W-OH)			
620		620		620		614			615		
705		702		704		708			710		
								₽ <b>W-O-W</b>	745	$\delta OD (W-OD)$ .	1.36
770	775	765	780	763	770	761	770		765		
835	840	838	840	835	830	820	830		820	A 1997 -	
		1						and shall be and the	840	$\delta$ OD (W-OD)	1.36
880	880	875	870	873	870	870	868		870		
			1			917	920	ν <b>W</b> —Ο	923		
941	940	936	940	935	940	934	935	(terminal)	940		
				950	950	952	953		955		
022		1015		1020		1020		δ OH (W-OH)			
						A State			1080	v <sub>4</sub> (ND <sup>+</sup> )	1.30
080		1090		1090		1090		?			
				1. 1. 1. 1.					1113	ND <sub>2</sub> H	
						1150		δ OH (W-OH)			
				2.44					1190	$ND_{3}H^{+}$	

									1205		$\delta$ OD (D <sub>2</sub> O)	1.356
									1261		$ND_2H_a^+$	
									1290		ND <sub>3</sub> H <sup>+</sup>	
									1350		?	
		1403		1403		1403		$v_4 (\mathrm{NH}_4^+)$	1403			
		SIL		1.00		1465			1460			
									1560		$D_2O$	1.346
1625	1630	1625	1635	1635	1630	1635	1630	δOH (H <sub>2</sub> O)				
				1660	1660	1678	1675	$\nu_2(\mathrm{NH}^+)$				
		2000-		2010-	_	2000-	_	4	2110			
2100		2190		2180		2100		H <sub>2</sub> O [27]	2210		ND <sup>+</sup>	
		1.50							2300		$v_3 (ND_4^+)$	1.366
									.2467	2460	νOD (W-OD)	1.370
									2572	2565		1.376
				No.					2662	2660	vOD (D <sub>2</sub> O)	1.352
						The second			2690	,	vOD (W-OD)	1.350
		2800		2800		2810		$2v_4$ (NH <sup>+</sup> )	2800			
		3020		3020		3020		$v_2 + v_4 \text{ (NH}^+_4)$	3010			
		3145		3140		3135		$v_3 (\mathrm{NH}^+)$	3120			
3300												
3380	3380	3370	3375	3360	3370	3380	3370	νOH (W-OH)				
3450		3460	3465	3466			1					
3540	3545	3555	3550	3550	3550	3540	3540	vOH (H <sub>2</sub> O)				
3577	3580	3580	3580	3580	3585	3600	3580		1.			
				A. S. Mark		3620	3630	vOH (W-OH)	S. A. Hora			
	Section Section					1000						

a: KBr pellet b: in

b: in Nujol or in hexachlorobutadiene



Fig. 4. IR spectra of (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> and WO<sub>3</sub>·H<sub>2</sub>O. 1. Ammonium chromate, anhydrous; 2. Ammonium chromate, deuterated; 3. Tungstene trioxide hydrate; 4. Tungstene trioxide hydrate, deuterated

experimental results cannot be reconciled with their chemical properties, e.g. with the experimental basicity of the salts.

The structure of the paratungstate ions has been determined first by LINDQVIST [9] for the substance of the composition  $5Na_2O \cdot 12WO_3 \cdot 28H_2O$ . According to this author, the crystal lattice of paratungstate consists of two discrete  $[W_{12}O_{46}]^{20-}$  ions per cell, instead of the  $[W_{12}O_{41}]^{10-}$  assumed earlier [10]. However, this structure requires the bonding of  $10H^+$  ions to the complex part, e.g. according to the formula  $[H_{10}W_{12}O_{46}]^{10-}$ , but this is inconsistent with the decidedly neutral character of the salt. SCHWARZMANN [11] and GLEMSER [7, 12] have concluded from IR and proton magnetic resonance measurements that the 10H atoms are not of acidic character, but participate in the structure of the anion by forming covalent OH groups. Accordingly, the formula  $[W_{12}O_{36}(OH)_{10}]^{10-}$ , most widely accepted at present, has been proposed by them for the structure of the ion; this is also in accord with the neutral character of the salt.

It had been shown by LIPSCOMB [13] already before one of the publications [7] of GLEMSER *et al.* that, in addition to  $[W_{12}O_{46}]^{20-}$ , another structure corresponding to the formula  $[W_{12}O_{42}]^{12-}$  could be derived from the results of LINDQVIST with the same probability. Its protonated form would be  $[H_2W_{12}O_{42}]^{10-}$ , which is more consistent with the crystallization of paratung-

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# Table III

Wavenumbers from the spectra of  $(NH_4)_2CrO_4$  and  $WO_3\cdot H_2O$ 

(NH4)2CrO4	(NH4)2CrO4 deuterated	Assignment	$WO_3 \cdot H_2O$	$WO_3 \cdot H_2O$ deuterated	Assignment	Shift ratio
	554		700	700	v W_0_W	-
No	750		1		1. 2. 10 10	-
780			1	-		1.11
843	843			1. 5. 6		1.7.5.
880						
938	940		1			
948			949	949	v W-0	
	1075	$v_{4}(ND_{+}^{+})$				1.347
	1120	ND <sub>o</sub> H <sup>+</sup>	1	a straight	and the second	
	1188	ND <sub>2</sub> H+			1	
1.1.1.1.1.1		0		1197	$\delta OD(D_2O)$	1.354
S	1260	1	-			
	1350	?		118	Sector Sector	
1408	1408	$v_{\rm A}({\rm NH^+})$				1 and
		4' 4'	1	1430	δHDO	
1458						1.
	1570					
Sist A		a management of a	1620	1620	$\delta OH(H_2O)$	
1655		$v_{2}(\mathrm{NH}^{+})$				
1750		$\nu_A + \nu_6$				
	2110			1		1.327
1. 1.	2200	ND <sup>+</sup>			and the second second	.1.372
	2330	$v_3(ND_1)$	1			1.357
		4,		2490	$v OD(D_2O)$	1.365
				2520	v HDO	
				2565	$v OD(D_2O)$	1.378
				2620		1.356
2800	2800	$2v_4(NH^+)$		i de la		
3000	3020	$v_2 + v_4(NH^+)$		1.12	- June in	
3163	3130	v <sub>3</sub> (NH <sup>+</sup> )			in and the	No.
	10 m		3400	3400		1.1.1
			3535		v OH(H <sub>2</sub> O)	
	1		3580	1.0	A States	1 1 1

states from nearly neutral media, than the structure proposed by LINDQVIST. Later, the X-ray diffraction analysis of ammonium paratungstate-11-hydrate by WEISS [14] verified the arrangement of W atoms found by LINDQVIST, but the determination of the O atom positions supported the hypothesis of LIPSCOMB.

On the basis of IR spectrophotometric investigations, several authors [15, 16] have come to the conclusion that the  $H_3O^+$  ions play an important part in the structure of sodium paratungstate. YUKHNEVICH [15] characterized the structure of the crystalline substance by the formula  $Na_{10}(H_3O^+)_{10-x}$ .  $[H_xW_{12}O_{46}] \cdot (4 + x)H_2O$ , in which the value of x small. Though the presence of  $H_3O^+$  ions is in general accepted by KEPERT [17] and SZARVAS [18] in their reviews, the conclusions of SPITSYN [19], based on this fact, were strongly criticized by KEPERT [17]. In contrast to this, the results of GLEMSER *et al.* [7] positively exclude the presence of  $H_3O^+$  ions in the crystalline phase.

The positions in the 7- and 5-hydrates have not been determined of the tungsten and oxygen atoms, only data on the dimension and symmetry of the unit cells are available [5, 20]. The character of the bonds of co-ordinated  $H_2O$  molecules to the anion is not clarified either.

Crystallographic characteristics of paratungstate hydrates								
Paratungstate	Crystal class	Space group	Z	Ref.				
Sodium paratungstate · · 28H <sub>2</sub> O	triclinic-pinacoidal	$PI - C_i^1$	2	[9]				
$\begin{array}{c} \mathbf{Ammonium} \text{ paratungstate } \cdot \\ \cdot 11\mathrm{H_2O} \end{array}$	rhombic-bipyramidal	Pbca — $D_{2h}^{15}$	4	[5, 14]				
Ammonium paratungstate · · 7H <sub>2</sub> O	triclinic-pinacoidal	$PI - C_i^1$	4	[5]				
Ammonium paratungstate · · 5H <sub>2</sub> O	monoclinic-prismatic	$P2_{1/a} - C_{2h}^5$	2	[5]				

## Table IV

The various hydrates have different crystallographic parameters (Table IV). The symmetry of both LINDQVIST's and LIPSCOMB's anion is  $C_{2h}$  according to Fig. 5. This identical symmetry notwithstanding, the two structures imply several essentially different consequences. As can be seen from Fig. 5 and Table V, the co-ordination conditions within the ions are different; LIND-QVIST links the four tritungstate groups exclusively through three-co-ordinate oxygen atoms, whereas LIPSCOMB includes both two- and three-co-ordinate atoms. The most important consequence is, however, that, owing to the dif-

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Fig. 5. Structure of the paratungstate ion. A. According to LINDQVIST ( $[W_{12}O_{46}]^{20-}$ ); B. According to LIPSCOMB ( $[W_{12}O_{42}]^{12-}$ )

Tabl	e	V
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Internal co-ordination in the paratungstate ions

Bond type of the oxygen atoms	Number of	bond types	Number of possible geometrical positions		
	LINDQVIST	LIPSCOMB	LINDQVIST	Lipscomb	
0 — (W <sub>3</sub> )	10	6	3	3	
$0 - (W_2)$	6	18	2	5	
$0 - (W_1)$	30	18	8	5	
0 - non-					
co-ordinated	23	27	?	?	

ferent number of  $O_{-}(W_1)$  bonds, the free octahedral positions capable of co-ordination in the external sphere of the ion, require different amounts of both the H<sup>+</sup> ions and of the OH or H<sub>2</sub>O groups, similarly to the metatungstates and the heteroanions of tunsgten [21].

It is therefore still open to debate whether one should accept LINDQVIST'S or LIPSCOMB'S basic structure as generally valid, or both the  $[W_{12}O_{46}]^{20-}$  and the more closely packed  $[W_{12}O_{42}]^{12-}$  basic structures are possible independently of each other. With the aid of thermocondensation [4] and spectrophotometric investigations we wish to contribute to the solution of this problem.

# b) Interpretation of the spectra

Similarly to the polymolybdates [22], the polytungstates too are difficult to study by molecular spectroscopic methods. The unit cells, best reflecting the symmetry properties, but also the polyanions proper contain many atoms, so that a great number of vibrations is to be expected on the basis of strict theoretical considerations. As compared to this, only a rather restricted number of bands is observed, which makes even an approximate assignment very difficult in the frequency region of W—O vibrations. A further limitation is imposed by the fact that the structure of paratungstates, studied by X-ray diffraction, is not yet cleared in every detail. For example, the positions of the Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions are unknown, and the position of the oxygen atoms has been determined experimentally only in a single case [14]. In the cells of the paratungstates, the W and O atoms are in a general position [9], which does not permit even an approximate discussion by means of site symmetry relevant to crystalline structures. Nevertheless, conclusions may be drawn, which bring us nearer to our goal.

From a comparison of the spectra in Figs 1 and 2 and of the data in Table II, it can be seen directly, that no essential difference is detectable between the spectra of paratungstates. Indeed, the frequencies of the W—O vibrational modes, the shapes of the bands and their intensity ratios are almost identical. Thus, we are confronted with the relatively rare case, in which the spectra of crystalline salts, represented by an identical chemical formula, are, to a very good approximation, independent of the point group symmetry of the crystal. It becomes evident from this that the forces holding together the crystal, *i.e.* the interactions between the molecules, are negligible compared to the forces acting within the molecules and the anions. Therefore, the paratungstate ion represents such a spectroscopically closed unit, in which the spatial differences of the environment in the crystal, *i.e.* the differences in the point group symmetry of the crystal, do not manifest themselves (at least in the frequency range investigated).

The splitting of the  $C_{2h}$  point group species relevant to the ions into factor groups according to Table IV is shown in correlation Table VI. Table VII is given as an example of the number of theoretically possible vibrational degrees of freedom and species, showing the results of the factor group analysis, performed for the paratungstate ion. Assuming that both the  $[W_{12}O_{46}]^{20-}$ and  $[W_{12}O_{42}]^{12-}$  formulas are possible (as well as those derived from them), the number of bands to be expected in the infrared and Raman spectra is, according to Table VII, somewhat different in the two cases. Similarly, differences would be expected also on the basis of Table V.

We have seen that the different symmetries of the elementary cells do not cause perceptible changes and the infrared spectrum is determined pri-

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#### **Table VI**

Splitting of the C<sub>2h</sub> point group species into species of crystal point groups



#### **Table VII**

Ion point group Crystal point group C2h  $C_i(Z=2)$ Number of degrees of Number of degrees of Irred. Irred. freedom freedom repr. repr. [W12O46]20-[W12O46]<sup>20-</sup>  $[W_{12}O_{42}]^{12} [W_{12}O_{42}]^{12}$  $44 + R_{-}$  $41 + R_{-}$  $A_g(R)$ 168 + 3 libr. 156 + 3 libr.  $A_{\mu}(R)$ +3 tr. + 3 tr.  $40 + T_z$  $37 + T_{z}$  $A_u(IR)$  $B_g(R)$  $40 + R_x, R_y$  $37 + R_r, R_r$  $A_u(IR)$ 168 + libr. 156 + libr. $44 + T_{x}, T_{y}$  $41 + T_r, T_s$  $B_{\mu}(IR)$ 

Final results of the factor group analysis of sodium paratungstate

marily by the structure of the paratungstate ion. Since the spectra do not exhibit differences, which would point in one case to the  $[W_{12}O_{46}]^{20-}$  and in the other to the  $[W_{12}O_{42}]^{12-}$  basic structure, the great similarity found in the frequency range (400—1000 cm<sup>-1</sup>) of the W—O vibrations supports the assumption that the compositions and structures of the paratungstate hydrate anions investigated are identical. This conclusion is essential from the point of view of further investigation, because if one of the two possible basic structures can be proved, the results must be considered as valid for every paratung-state.

For the assignment of the W—O vibrations according to Table II, the approximation is sufficient for us that the stretching frequencies of the terminal M=O or M—O bonds are always higher than those of the M—O—M type bridges in the various lattice layers [22–26]. For the case of polymolyb-dates, several considerations supported the assumption that the frequency range of the M—O(I) bonds should fall between 910 and 955 cm<sup>-1</sup> [22].

Let us now investigate in the following, how far the presence of OH or more exactly W-OH groups and possibly that of H<sub>3</sub>O<sup>+</sup> ions besides the presence of H<sub>2</sub>O groups is supported by the spectra. It is noticeable that small inflections or individual maxima are exhibited in the high-frequency region of the wide vOH bands between 3580 and 3630 cm<sup>-1</sup>. This finding may be interpreted in general by the formation of H<sub>2</sub>O groups coordinated through very weak hydrogen bonds, or possibly of free OH groups [27, 28], or W-OH groups [15, 28, 30]. In the case of the 5-hydrates, the band at 3630 cm<sup>-1</sup> corresponds to the frequency of the free OH groups (the O ... O distance is 3.1 Å). It is apparent from Fig. 1 and Table II that the maximum at 555 cm<sup>-1</sup> disappears on deuteration, so that the band can be attributed to an OH vibration, while the low frequency of this band is indicative of the  $\delta OH$  vibrational mode of the free OH groups [28]. With increasing hydrate content, the intensity of the maximum in the immediate vicinity of 555 cm<sup>-1</sup> decreases gradually, in the 11-hydrate it becomes barely perceptible, while it does not appear at all in the 28-hydrate. This finding supports the assignment of the given band, because the extension of the hydrate shell around the anion reduces the number of free OH groups bonded to tungsten or completely eliminates them owing to the formation of hydrogen bonds. Between 1000 and 1200 cm<sup>-1</sup>, *i.e.* in the frequency region where the  $\delta OH$  bending vibration bands of the hydroxo groups covalently bonded to the metal (M-OH...) and involved also in hydrogen bonding are exhibited [25, 27, 28, 31], very weak maxima can be observed. The identification of these bands would also prove decisively the presence of structural OH groups in the paratungstate ion. In the spectrum of the deuterated 5-hydrate, very weak new maxima appear at 745 and 840 cm<sup>-1</sup>, superimposed on the vW-O-W bands. For these, the band shift ratio verifies the association with the  $\delta$ OH bands at 1020 and 1150 cm<sup>-1</sup>. In the OH stretching vibration region, the vOH band of the W-(OH) ... O bond type lies probably in the range of 3360-3380 cm<sup>-1</sup> [25, 28].

The presence of water molecules in the crystalline phase is unambiguously proved by the spectra and this fact cannot be doubted even in the case of the 5-hydrates. The bond at 1600 and 1700 cm<sup>-1</sup>, in the frequency range of  $\delta$ OH(HOH), is split into two bands in the case of the 7- and 5-hydrates, and a new maximum is observed between 1660 and 1680 cm<sup>-1</sup>. This might easily suggest the presence of  $H_3O^+$  groups, however, a more detailed analysis rules out this assumption, in accordance with the findings of GLEMSER *et al.* [7]. A comparative analysis of the four IR and Raman active fundamental vibrations of the pyramidal  $(C_{3\nu})H_3O^+$  [31—36] and  $D_3O^+$  [33, 35, 37], of the absorption frequencies of the partially deuterated ions [37], and of the data in Figs 1, 2 and Table II, provides no conclusive evidence for the presence of  $H_3O^+$  ions. At the same time, the interpretation of the spectral bands is free of contradictions with only  $H_2O$  and OH groups taken into consideration.

It is much more likely that the band between 1660 and 1680 cm<sup>-1</sup> arises from the vibration of the  $NH_4^+$  ion, since this band is exhibited also in the spectrum of the anhydrous  $(NH_4)_2CrO_4$ . Presumably, the band is due to the  $v_2$  vibrational mode, otherwise forbidden in the infrared, which, owing to the symmetry or distortion of this ion in the crystal lattice, becomes infrared active in both compounds.

On deuteration, a rather complicated system of OH—OD, NH—ND bands is formed, however, orientation is greatly assisted by the data in Table III. The identification of the vibrational bands of the  $ND_4^+$ ,  $ND_3H^+$  and  $ND_2H_2^+$  groups is facilitated by the fact that these frequencies have been identified for various deuterated ammonium salts by several authors [37, 38].

The splitting of the vW—O band of the W—O groups observed upon decreasing hydrate contents would still call for some explanation (Fig. 1, Table II). As concerns the whole of the system, Correlation Table VI does not give unequivocal information on this problem, though in the correlation  $C_{2h} \rightarrow$  $\rightarrow D_{2h}$  the number of bands actually decreases in the case of the 11-hydrate as compared to the 7- and 5-hydrates, owing to the inactivity of the  $A_u$  species. The answer is less evident with respect to the  $C_{2h} \rightarrow C_i$  correlations, particularly when we take into consideration the Z values characteristic of the contents of the unit cells. A possible interpretation by a more primitive approach is that, with decreasing hydrate content, W—O(I) bonds of different type and strength in the anions manifest themselves to an increasing extent in the splitting of the spectral band. According to the character of the chemical bonds of the OH and H<sub>2</sub>O groups in the paratungstate ion, in principle four kinds of W—O(I) bonds can be distinguished:

1. free W—O(I) group 950—953 cm <sup>-1</sup>	$\begin{array}{c} 0 0 \\ 0 - [\mathbf{W} - 0(\mathbf{I})] \\ 0 0 \end{array}$
2. W—O(I) group with co-ordinated H <sub>2</sub> O 934—941 cm <sup>-1</sup>	0 0 0-[W-0]НОН 0 0
3. free W—OH group $\sim$ 918 cm <sup>-1</sup>	0 0 0-[W-0]H 0 0
4. W—OH group with co-ordinated $H_2O < 918 \text{ cm}^{-1}$ ?	$\begin{array}{c} 0 & 0 \\ 0 & -[W-0] H 0 H_2 \\ 0 & 0 \end{array}$

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With the decrease of the hydrate sheath surrounding the anion, the groups become more and more differentiated, and this causes a certain separation of the vibrational bands of the different W-O(I) bonds. When the co-ordination sphere of the ion contains an adequate number of water molecules, the stretching vibrations of free W-O and [W-O] H cannot be detected. Thus, e.g., in the spectra of the 28- and 11-hydrates, the absorption collapses into a single band, owing to the predominance of the [W-O]...... HOH bonds. The reduced size of the hydrate sheath favours the formation of free W-O(I) groups, and their stretching frequency appears first in the spectrum of the 7-hydrate. In the case of the 5-hydrate, a new maximum is observed at 918  $\rm cm^{-1}$ , which can be attributed to further differentiation of the groups, thus to the independent appearance of the [W-O]H groups. On deuteration, a slight shift towards higher frequencies of the W-O(I) bands can be observed. In view of the fact that the exchange of the hydrogen bonded protons for deuterium may increase the 0... 0 distance by 0.02--0.04 Å [25, 40], the W-O distance is shortened obviously because of the decreased strength of the hydrogen bond, which produces a slight shift of the band system of the W-O(I) bonds towards higher frequencies.

# c) Conclusions concerning the structure

According to the spectral studies it can be established that independently of the hydrate content and of the co-ordinating Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup> ions, the paratungstate ion has an identical structure. It is rather improbable that the basic structure would be  $[W_{12}O_{46}]^{20^-}$  in one case, and  $[W_{12}O_{42}]^{12^-}$  in the other. It is also clear that paratungstates contain, in addition to differently co-ordinated water molecules, smaller quantities of structural OH groups. Therefore, a decision concerning LINDQVIST's or LIPSCOMB's basic structure is to be expected from experimental data on the quantitative relation of OH and H<sub>2</sub>O groups.

If the formula  $[W_{12}O_{36}(OH)_{10}]^{10-}$ , deduced from the basic structure  $[W_{12}O_{46}]^{20-}$  were accepted as valid, the general formula of paratungstate should be written as follows:

$$5R_2O \cdot 12WO_3 \cdot nH_2O = R_{10}[W_{12}O_{36}(OH)_{10}] \cdot mH_2O$$

where n is 28, 11, 7 and 5, m is 23, 6, 2 and 0, R is  $NH_4^+$ ,  $K^+$ ,  $Na^+$ .

Consequently, the 5-hydrate and its dehydrated products would not at all contain  $H_2O$  (W-O... $H_2O$ ) co-ordinated as molecular water. This, however, is inconsistent with our earlier [4] and present spectrophotometric investigations, as the distinct appearance of the  $\delta OH(H_2O)$  bands in the spectrum of the 5-hydrate and even in the spectra of hydrates containing less water

constitutes decisive proof. In accordance with this finding, it has been established in our thermocondensation experiments combined with structural investigations that at least 3 moles of molecular water are co-ordinated to the anion of the 5-hydrate [4]. It has been shown that the removal of 3H<sub>2</sub>O, *i.e.* the dehydration process 5-hydrate  $\rightarrow$  2-hydrate proceeds without a change of structure [4], which excludes the presence of 10 structural OH groups in the anion. Similar results were obtained in the investigation of the thermolysis of sodium paratungstate, where up to the loss of 26 moles of H<sub>2</sub>O, *i.e.* until the formation of 2-hydrate, no essential structural changes have been observed [41].

It can be established in summary that, in the light of the results of several methods, only LIPSCOMB's basic structure is consistent with the experimental findings. The structure  $[W_{12}O_{42}]^{12-}$  has been proposed only as a hypothesis by LIPSCOMB on the basis of the measurements of LINDQVIST. Later it has been verified by WEISS in a concrete case, while our thermocondensation and IR spectrophotometric measurements have extended its validity as the general formula for all paratungstates studied in this work.

However, the LIPSCOMB-WEISS structure still requires modifications. Namely, according to our earlier [4] and present experiments instead of  $[H_2W_{12}O_{42}]^{10-}$  the structure of the anion corresponds to the formula  $[W_{10}O_{10}(OH)_{2}]^{10-}$  which is consistent with the results of thermal and spectral analyses, as well as with the decidedly neutral character of the salt. Since there is no indication that the structure of the basic compounds investigated would be substantially different within the hydrate range from 28 to 5H<sub>2</sub>O in the analytical sense, we propose the following formula as the general formula of paratungstates:

$$M_{10}[W_{12}O_{40}(OH)_2] \cdot mH_2O, \quad ext{ where } M = \operatorname{Na}^+, \ \operatorname{K}^+ ext{ and } \operatorname{NH}_4^+, \ ext{ and } m = 27 - 4.$$

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# REDUCTION AND OXIDATION OF ACETALDEHYDE AND PROPIONALDEHYDE ON PLATINIZED PLATINUM ELECTRODE

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The electrohydrogenation and electrooxidation of acetaldehyde and propionaldehyde have been investigated in acidic solution  $(1N \text{ HClO}_4)$  on a platinized Pt electrode. It has been found that in the electrohydrogenation process considerable amounts of ethane and propane are formed, whereas oxidation processes yield the corresponding carboxylic acids. The difficulties in determining steady-state polarization curves have been pointed out.

Problems concerning the electrochemical oxidation and reduction of aldehydes, generally oxo compounds, attracted considerably attention already in the very early stages of electrochemistry [1, 2]. One might think that by now, regarding first of all experimental facts, the topic has been exhausted. This is, however, not the situation, as is indicated by recent investigations concerning the reduction, i.e. electrohydrogenation, of aliphatic ketones [3, 4] on platinized Pt electrodes. Contrary to views accepted for many decades, it has been established that aliphatic ketones, first of all acetone and methyl-ethyl ketone, can easily be hydrogenated on platinum electrodes, the main products being the corresponding hydrocarbons. This observation indicated that, presumably, the same phenomenon may appear in the case of aldehydes too, so a renewed interest has emerged in the hydrogenation and electrohydrogenation of some simple aldehydes, e.g. acetaldehyde and propionaldehyde. Moreover, for investigations on the electrooxidation of primary alcohols, the elucidation of the redox properties of the corresponding aldehydes appears to be indispensable.

This paper reports some of our investigations aimed at the above problems.

# 1. Reduction of acetaldehyde and propionaldehyde

Based on the investigations of steady-state and transient processes involved in the electrochemical reduction of aldehydes, the following important statements are described in the pertinent literature:

1) Aliphatic aldehydes do not undergo reduction on platinum metals.

2) Aldehydes can be converted to hydrocarbons (e.g. propionaldehyde

to propane) only at substantially more negative potentials than the potential of hydrogen evolution.

3) Accordingly, aldehydes can be reduced to hydrocarbons only on electrodes of high hydrogen overvoltage.

In the light of these statements the investigation of the electrohydrogenation of aldehydes on platinum electrode appears to be meaningless. On the other hand, if one studies the thermodynamics of the following reaction type (where R denotes an alkyl group)

$$R-C-H+4H^++4e \rightarrow R-CH_3+H_2O$$
,

it can be established by simple calculations [5] that in the case of aliphatic aldehydes the standard redox potentials of the above reactions are around E = 300 mV. Hence, it is thermodynamically possible to convert aldehydes into hydrocarbons at potentials more positive than the potential of hydrogen evolution. From this point of view the situation is essentially the same for acetone and other ketones. On the basis of these considerations, investigations on the hydrogenation (electrohydrogenation) of aldehydes in acidic medium do not appear entirely hopeless.

# Experimental

The measurements were carried out in cell types commonly used in the practice of electrochemistry (see Fig. 1). As background solution, 1N HClO<sub>4</sub> was used. The electrode potential was measured against a 1 atm hydrogen electrode immersed into the same solution. With regard to the need for gas



Fig. 1. The cell used for electrolysis. A: main electrode; B: auxiliary electrode; C: reference electrode; V: junction to the gas burette

volumetric measurements the main electrode was separated from the auxiliary and reference electrodes by well sealable glass joints. The gas space of the cell compartment with the main electrode was attached to a gas burette.

# Results

The polarization curve  $(i_R)$  determined by the potentiostatic method in the presence of 0.3 mol/1 propional dehyde is shown in Fig. 2. For comparison, the cathodic polarization curve recorded in the background under N<sub>2</sub> is also



Fig. 2. Cathodic polarization curves;  $i_{H_2}$ : background solution (1N HClO<sub>4</sub>),  $i_R$ : 0.3 mol/1 propionaldehyde solution

presented. (The geometric surface of the sooted electrode was about 100 cm<sup>2</sup>.) It appears from the curve that the reduction of the aldehyde takes place at an appreciable rate only at potentials more negative than 60 mV. It should be noted that, at a given potential, the reduction rate decreases with time, and after a longer period (a few hours) the  $i_R$  curve turns into the  $i_{H_z}$  curve, *i.e.* the hydrogenation of the aldehyde ceases. The variation of current density with time (at 20 mV) is given in Fig. 3. At the electrode gas evolution can be observed; on the basis of gas chromatographic analysis it proved to be propane. Among the gaseous products no other hydrocarbons appeared in concentrations higher than  $1-2^{0}/_{0}$ .

In the case of acetaldehyde essentially the same phenomena were found; in this case ethane formation was observed. On the basis of the above experiments it can be stated that

1) The electrohydrogenation of aldehydes can be carried out on platinized platinum electrodes,

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2) among the products of hydrogenation the corresponding hydrocarbons also occur.

In order to find the proportion of the hydrocarbon components further experiments had to be carried out. The determination of current efficiency for the hydrocarbon can be made by volumetric measurements of the evolved gas under galvanostatic conditions, obviously, at potentials where no appreciable hydrogen evolution is expected.



Fig. 3. Current intensity vs. time at 20 mV

Reference measurements were carried out for avoiding the possiba errors. In the absence of aldehyde the background electrolyte was electrolyzdwith the same electrode and current density as used in the electrohydrogenee tion of the aldehyde, and the volume of the hydrogen evolved was measured.

According to the reaction  $2H^+ + 2e^- \rightarrow H_2$ , a charge of 2F is required for the formation of 1 mol of hydrogen, whereas the formation of 1 mol of hydrocarbon requires 4F.

The volume vs. time curves for propionaldehyde are shown in Fig. 4. In the presence of aldehyde the electrode potential never became more negative than 30 mV, so the amount of hydrogen in the gases evolved was a few per cent at the most. Bearing this in mind, the slight curvature of the curve referring to  $CH_3$ — $CH_2$ — $CH_3$  can be explained by assuming that in the progress of electrolysis another product may also be formed (e.g. alcohol) in addition to propane. Anyhow, it is apparent from the example presented here that the current efficiency with respect of the hydrocarbon is, at the beginning of the electrolysis, nearly 100%. (The slope of curve 2 at the origin is about one half of that of curve 1.)

Considering the above, it can be said that in the electroreduction of aliphatic aldehydes a considerable amount of hydrocarbons is formed.

This experimental fact disproves the opinion, existing for great many years, that aldehydes can be reduced to hydrocarbons only at electrodes of high hydrogen overpotential.



Fig. 4. Gas volume vs. time at a current of 15 m A: background solution 1N HClO<sub>4</sub>, 0.3 mol/1 propionaldehyde solution



Fig. 5. Polarization curve for 0.3 mol/l acetaldehyde

HORÁNYI, NOVÁK: REDUCTION AND OXIDATION OF ACETALDEHYDE

Difficulties arise, though, in establishing a potential-current relationship for the electrohydrogenation, owing to the very narrow potential range and to the variation of the reaction rate with time. In potentiostatic measurements on acetaldehyde, if the potential is changed between two measurements relatively quickly, the curve given in Fig. 5 can be drawn from the measured current intensity data, *i.e.* the log *i vs.* plot is approximately a straight line with a slope of about  $1/60 \text{ mV}^{-1}$ . The situation is similar with propionaldehyde (Fig. 6), only the slope being different  $(1/80 \text{ mV}^{-1})$ . As far as we see, the reli-



Fig. 6. Polarization curve for 0.3 mol/l propionaldehyde

ability of these data is insufficient for making any definite conclusions from the slope data on the detailed mechanism of hydrogenation. At any rate, it appears probable that the reduction takes place *via* a "radical mechanism" [6], *i.e.* the hydrogen atoms adsorbed on the platinum take part in the reaction.

# 2. Investigations on the oxidation

Together with the oxidation of ethanol also the oxidation of acetaldehyde was studied by HOLLNAGEL and LOHSE [7], as well as by RIGHTMIRE *et al.* [8]. It has been found that the product of the oxidation is acetic acid. In potentiostatic measurements a current maximum has been observed at about 1200 mV. In the case of ethanol this maximum appears around 850 mV.

This difference between the oxidation of alcohols and aldehydes has been attributed by HOLLNAGEL and LOHSE to the oxide layer on the surface, which, in the case of ethanol inhibits the reaction, whereas in the case of the aldehyde this does not occur because of the reaction

$$PtO + CH_3CHO \rightarrow CH_3COOH + Pt.$$

No investigations have been found in the literature concerning the behaviour of the higher members of the homologous series of aliphatic aldehydes. For the study of the oxidation of n-propanol, however, as it has been mentioned, the investigation of the oxidation of propionaldehyde was necessary.

Our first investigations aimed at the determination of the oxidation products. A very simple indirect method, also applicable in other similar cases, was used to determine if products other than propionic acid were formed in the process. In the cell, connected to a gas burette, oxidation was carried out for a long time at a relatively high current (200 mA for 1 to 2 hours). If the oxidation yielded products other than propionic acid, gaseous products should also be formed, which would be indicated by the gas burette. In the experiments no change of the gas volume was observed, so it can be stated that products, apart from propionic acid, were formed only in negligible amounts. (The same experiment was carried out also with *n*-propanol, and no gas evolution was observed in this case either; so the analogy with ethanol, at least in this respect, is complete.)

During the galvanostatic measurements the potential was not exactly constant, changing between 1000 and 1300 mV, so the above statements pertain to these fairly high potential values and broad potential range.

In order to determine the steady state polarization curve for the oxidation process, the question had to be answered if the steady state can be achieved at all.

The variation of the current with time at different potential values (for propionaldehyde) measured by a potentiostatic method is shown in Fig. 7. The measurements started at low potential values, and the potential was gradually increased, allowing 20 to 40 min between the consecutive measurements.

It can be seen from the figure, that the attainment of a steady state, particularly at potentials more positive than 1000 mV, can hardly be assumed.

In accordance with the phenomena observed in the case of acetaldehyde [7], it has been found that in the present case, too, the potential dependence of the rate of oxidation corresponds to a curve with a maximum, provided that the time elapsed between the experiments is longer than 5 min but does not exceed 40 min. The maximum is around 1200 mV also in this case. On the basis of Fig. 7 it is also clear that several different polarization curves may be constructed, depending on the time elapsed between the experiments, so by this method the unequivocal determination of the polarization curve is impossible.

In our opinion, the time dependence of the current at fixed potentials is related to the slow formation of an oxide layer. According to our investigations reported elsewhere [9], the rate of reactions in which oxygen adsorbed



Fig. 7. Variation of current with time in the potentiostatic measurements; 0.3 mol/l propionaldehyde solution

on platinum (oxide) takes part is low, so in the case under study, even at high positive potentials, it is the free metal surface that takes part in the reaction. This provides an explanation for the diversity of polarization curves and the uncertainty of their determination.

It is clear from the above considerations that the more exact interpretation of these phenomena does require further investigations.

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# THERMODYNAMIC FUNCTIONS OF ISOTOPIC DIBORANE MOLECULES

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Thermodynamic functions of isotopic diborane molecules are calculated using spectroscopic data and assuming the rigid rotator harmonic oscillator approximation. The functions  $C_{mp}^*$ ,  $S_m^*$ ,  $(H_m^* - E_{m0}^*)/T$  and  $-(G_m^* - E_{m0}^*)/T$  are given for 100 to 1000 K.

CYVIN and VIZI [1] carried out normal co-ordinate analyses of isotopic diborane molecules and calculated the mean amplitudes on the basis of experimental data from the literature. It turned out eventually that the relative magnitudes for two stretching force constants used in Ref. [1], seemed to be unreasonable. Therefore the force field had to be revised [2]. In connection with the force field revision, the authors of the present work performed a calculation of the thermodynamic functions for isotopic diborane molecules. The calculations are based on the same structural parameters as in Ref. [1], and on vibrational frequencies [1, 3, 4]. The frequencies for  ${}^{11}B_{9}H_{6}$  and  ${}^{10}B_{9}D_{6}$ are identical with those in Ref.[1]. For the intermediate isotopic molecules the spectroscopic data, quoted by KUCHITSU in private communication [4], were taken from the work of OGAWA and MIYAZAWA [4]. The applied values for two lacking frequencies, viz. [954] and [1012] in Table I, were estimated from isotopic shifts according to KUCHITSU's calculation [3]. Symmetry species designation is in accordance with Refs [1] and [5]. The calculation was carried out in the usual way [6]. The results in Tables II-V are valid for the ideal gas state at atmospheric pressure.

### VIZI, CYVIN: THERMODYNAMIC FUNCTIONS

# Table I

	<sup>11</sup> B <sub>2</sub> H <sub>6</sub>	<sup>19</sup> B <sub>2</sub> H <sub>6</sub>	<sup>11</sup> B <sub>2</sub> D <sub>6</sub>	<sup>10</sup> B <sub>2</sub> D <sub>6</sub>
Ag	2524	2537	1850	1860
	2104	2110	1500	1511
	1180	1186	915	929
	794	820	700	726
B <sub>1g</sub>	1012	[1012]	730	730
B <sub>2g</sub>	2591	2640	1975	1980
	920	930	725	740
$\mathbf{B}_{3g}$	1768	1768	1270	1273
	1035	1044	860	870
A <sub>u</sub>	829	829	592	592
$\mathbf{B}_{1u}$	2525	2528	1840	1845
	1602	1606	1199	1205
	1177	1181	873	881
B <sub>2U</sub>	1915	1920	1460	1465
	973	977	720	728
	2612	2625	1985	1999
$\mathbf{B}_{3u}$	950	[954]	730	705
	368	368	250	262

Observed frequencies for isotopic species of diborane  $(cm^{-1} units)$ 

C.	(in cal $\cdot$ mol <sup>-1</sup> K <sup>-1</sup> units)								
Т, К	C*p	$\frac{\mathbf{H}_{m}^{*}-\mathbf{E}_{m}^{*}}{\mathbf{T}}$	$-\frac{\mathbf{G}_{m}^{*}-\mathbf{E}_{m}^{*}\mathbf{O}}{\mathbf{T}}$	$S_m^*$					
100	8.238	8.002	36.683	44.686					
200	9.996	8.489	42.351	50.839					
300	13.392	9.526	45.970	55.496					
400	17.224	10.974	48.903	59.876					
500	20.760	12.584	51.523	64.107					
600	23.866	14.212	53.962	68.173					
700	26.549	15.787	56.272	72.059					
800	28.843	17.280	58.478	75.758					
900	30.790	18.676	60.595	79.271					
1000	32.438	19.972	62.631	82.602					

## Table II

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# Table III

Calculated thermodynamic quantities for  ${}^{10}B_2H_6$ (in cal  $\cdot$  mol<sup>-1</sup> K<sup>-1</sup> units)

т, к	C <sup>*</sup> <sub>mp</sub>	$\frac{\mathbf{H}_{m}^{*}-\mathbf{E}_{m}^{*}0}{\mathbf{T}}$	$-\frac{\mathbf{G}_{m}^{*}-\mathbf{E}_{mo}^{*}}{\mathbf{T}}$	Sm
100	0 927	9 002	26 254	44 256
200	9.957	8.481	42.020	44.550
300	13.309	9.499	45.633	55.132
400	17.128	10.931	48.555	59.486
500	20.662	12.530	51.165	63.695
600	23.769	14.151	53.593	67.743
700	26.454	15.721	55.893	71.614
800	28.751	17.210	58.091	75.301
900	30.702	18.604	60.199	78.803
1000	32.354	19.899	62.227	82.126
1000		1.1.1		

#### **Table IV**

т, к	C*p	$\frac{\mathbf{H}_{m}^{*}-\mathbf{E}_{m0}^{*}}{\mathbf{T}}$	$-\frac{\mathbf{G}_{m}^{*}-\mathbf{E}_{m}^{*}\mathbf{O}}{\mathbf{T}}$	$S_m^*$
100	8.759	8.157	38.674	46.831
· 200	11.995	9.142	44.582	53.725
300	16.974	10.914	48.604	59.518
400	21.657	13.028	52.030	65.059
500	25.591	15.160	55.168	70.328
600	28.789	17.175	58.112	75.287
700	31.351	19.024	60.901	79.925
800	33.391	20.697	63.552	84.250
900	35.016	22.201	66.079	88.280
1000	36.317	23.550	68.489	92.039
	1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1. 1		CALIFORNIA STATE	The second se

Calculated thermodynamic quantities for  ${}^{11}B_2D_6$ (in cal  $\cdot$  mol<sup>-1</sup> K<sup>-1</sup> units)

-	-		
	1.1		57
1.3	n	P	v

Calculated thermodynamic quantities for  ${}^{10}B_2D_6$ (in cal  $\cdot$  mol<sup>-1</sup> K<sup>-1</sup> units)

Т, К	C <sup>*</sup> <sub>mp</sub>	$\frac{\mathbf{H}_{m}^{*}-\mathbf{E}_{m}^{*}o}{\mathbf{T}}$	$-\frac{\mathbf{G}_m^*-\mathbf{E}_m^*o}{\mathbf{T}}$	$S_m^*$
100	8.694	8.132	38.408	46.540
200	11.901	9.092	44.290	53.382
300	16.853	10.843	48.288	59.131
400	21.531	12.944	51.692	64.636
500	25.471	15.068	54.809	69.878
600	28.680	17.079	57.737	74.816
700	31.253	18.927	60.510	79.437
800	33.304	20.601	63.149	83.750
900	34.939	22.107	65.664	87.770
1000	36.249	23.458	68.064	91.522

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# ELECTRON DIFFRACTION INVESTIGATION OF ETHANE-1,2-DITHIOL

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The molecular geometry and rotational isomerism of ethane-1,2-dithiol was studied in the vapor phase by electron diffraction. Anti and gauche conformers were found about the C—C bond with relative abundances of 62 and 38 per cent, respectively. The gauche conformer can be obtained from the anti form by rotating one of the SH groups about the C—C bond by  $106^{\circ}$ .

## Introduction

A vibrational analysis was carried out by HAYASHI, SHIRO, OSHIMA and MURATA [1] to study the rotational isomerism and force constants of ethane-1,2-dithiol, HS— $CH_2$ — $CH_2$ —SH. They found two simultaneously existing conformers in the gaseous state, *anti* and *gauche*, about the C—C bond with an energy difference of 0.63 kcal/mol, the *anti* form being more stable. Other 1,2-disubstituted ethane derivatives have been and are extensively studied both by spectroscopy and electron diffraction (see e.g. Ref. [2]). For a comparison with the spectroscopic results and also to provide the molecular geometry for further force model investigations we undertook a study of the structure and rotational isomerism of ethane-1,2-dithiol in vapor phase by electron diffraction.

# Experimental and data reduction

Ethane-1,2-dithiol (b.p. 146  $^{\circ}$ C/760 mm) is a colourless liquid and has extremely offensive odour. The sample used in this study was the product of the Chemical Samples Co. (Columbus, Ohio, U.S.A.).

The electron diffraction patterns were recorded on the Budapest apparatus described earlier (a modified EG-100A unit) using newly designed nozzle [3] and sector [4] systems. Nozzle to plate distances of 50 and 19 cm and 60 keV electrons were utilized. The nozzle temperature was about 70 °C during the experiment. Four and three plates from the long and short camera distances, respectively, were chosen for analysis. A Zeiss GIII photometer was used for obtaining the optical density distributions. The plates were oscillated around the centre of the diffraction pattern during the tracing. The ranges of intensity data were  $1.75 \le s \le 12.25$  Å<sup>-1</sup> and  $7.00 \le \le s \le 30.25$  Å<sup>-1</sup>, respectively ( $s = 4\pi\lambda^{-1}\sin 1/2 \Theta$  where  $\lambda$  is the electron wavelength and  $\Theta$  is the scattering angle).

For drawing the first experimental background, theoretical molecular intensity curves were taken into consideration. Therefore, preliminary curves were calculated for anti and gauche isomers and their mixtures with assumed geometry. The experimental molecular intensities were obtained according to the expression  $sM^{E}(s) = s[I(s) - B(s)]/B(s)$  in the usual way. Here I(s)are the total experimental intensities and B(s) the experimental background. The latter was later modified when better theoretical curves became available. The final versions are shown in Fig. 1. The experimental molecular



Fig. 1. The total experimental intensities,  $I_{\ell}^{E}(s)$ , for the 50 cm and 19 cm camera range, shown with the experimental background drawn in



Fig. 2. Molecular intensities. E — experimental; T — theoretical, corresponding to the geometry presented in Table II and a 62 and 38 per cent mixture of *anti* and *gauche* conformers. The difference ( $\Delta$ ) between E and T is also shown

intensities were scaled and averaged to form a single composite curve shown in Fig. 2 and corresponding to the equation

$$sM(s) = \sum_{\substack{i \ i \neq j}} \sum_{j} rac{|f_i(s)| |f_j(s)|}{B(s)} \cos \left[\eta_i(s) - \eta_j(s)
ight] imes \ imes \exp\left(-rac{1}{2} l_{ij}^2 \, s^2
ight) \sin (r_{ij} \, s)/r_{ij}$$

where the |f(s)| and  $\eta(s)$  are the absolute values and phases of the complex electron scattering amplitudes, the  $r_{ij}$  are interatomic distances and the  $l_{ij}$ are the corresponding mean amplitudes of vibration; the summation extends over all atomic pairs. The numerical values of the composite experimental molecular intensity curve are listed in Table I.

Table IExperimental molecular intensity data, range s = 1.75 by 0.25 to 30.25 Å<sup>-1</sup>(arbitrary scale)

- 961	-2380	-2948		—1691	
- 964		-1533	- 946	542	2013
2876	2510	1537	619	- 419	
2671	-2507	-1214	816	2631	3303
2009	477	— 566	— 731	— 520	- 215
- 488	— 981	-1522	-1345		- 657
— 21	1105	2508	3120	2896	1394
— 549	-1856	-2651	-2301		- 617
798	1781	2432	2256	1415	70
-1021	-1282	-1265	-1299	— 974	-1094
-1113	- 728	- 192	502	1135	1904
2668	2562	1695	615	— 905	
-2478		-1160	- 302	109	724
631	817	544	201	167	- 304
258	- 446	- 651	- 852	-1245	- 735
- 551	314	338	633	743	901
605	70	— 533	- 672	-1222	- 502
- 829	— 558	657	94	334	579
827	392	98	- 249	302	- 220
-1095	and the				

The table develops horizonllaly

### Structure analysis

Geometry of the models. If assuming that the S—H bonds are anti to the C—C bond<sup>\*</sup>, and the SCC planes bisect the HCH angles, the geometry of the anti conformer about the C—C bond can be described by four bond lengths (C—H, S—H, C—C, S—C), and four bond angles (S—C—C, C—S–H, H—C—H and S—C—H). For determining the geometry of the gauche form, an additional parameter, the torsional angle from the anti form  $\tau$ (S—C—C—S) is needed implying that the two conformers have the same bond lengths and bond angles. The representation of the torsional angle is given in Fig. 3.



Fig. 3. Representation of the torsional angle  $\tau$ 

Experimental radial distribution. The experimental radial distributions were calculated from the experimental molecular intensity data. Either zeros or theoretical sM(s) values were used for the unobserved range  $0.25 \le s \le 1.50$ Å<sup>-1</sup>. The experimental radial distribution curve in Fig. 4 was computed using a damping factor a = 0.002 Å<sup>2</sup> and the values of the theoretical intensity curve of Fig. 1 for the unobserved range. For this and other calculations the partial waves electron scattering amplitudes and phases obtained by STRAND's program [5] were used.

The three peaks between 1 and 2 Å on the experimental radial distribution curve arise from the bond distances C—H, S—H, C—C and S—C. The peak at 1.1 Å is due to the C—H bond distances, the next one at 1.5 Å is built up by contributions from the S—H and C—C bonds and is unresolved. The S—C bond appears at about 1.82 Å. The maxima between 2 and 3 Å correspond to non-bond distances. The most important of these are the S.C distances\*\* which are independent of rotation about the C—C bond. The major

\* This assumption is supported by the considerations presented by HAYASHI et al. [1]. \*\* Here and hereafter the number of dots specifies the number of bond angles separating the atoms.

#### SCHULTZ, HARGITTAI: ELECTRON DIFFRACTION INVESTIGATION



Fig. 4. Radial distributions. E — experimental. The theoretical curves correspond to the geometry presented in Table II with A — all anti; G — all gauche; and 62 + 38 per cent anti and gauche conformers. The difference ( $\Delta$ ) between E and 62% A + 38% G is also shown

contributions to the maxima at about 3.5 and 4.4 Å come from the S. . S non-bond distances in the gauche and anti conformers, respectively.

Trial structures. The starting values for the C—H, S—H, C—C and S—C bond distances were 1.09, 1.35, 1.54 and 1.80 Å, respectively. The bond angle C—C—S was estimated to be 113.5° using the mentioned values for the C—C, S—C bonds and the value of the maximum at 2.8 Å, to which the main contribution comes from the S.C distances. The other angles around the carbon atoms were assumed to be tetrahedral, the sulfur valence angle was estimated to be 100°. The maximum for the gauche S..S distances at about 3.5 Å was also taken into account in estimating the  $\tau$  torsional angle to be 114°. Concerning the amounts of the conformers, a series of theoretical radial distributions were calculated at this early stage with different ratios including the one (56% anti and 44% gauche) corresponding to the energy difference obtained in the vibrational analysis by HAYASHI et al. [1]\* The radial distributions were rather insensitive to this ratio and the spectroscopic results were used as starting values for the amounts of the conformers in most cases at this stage of the analysis. The starting values of the mean amplitudes of vibration were

<sup>\*</sup> The  $n_g/n_a = 2(f_g/f_a) \exp(-\Delta E/RT)$ , (2), formula was used where  $n_g/n_a$  is the molecular ratio for the two forms, 2 is the weight factor of the gauche form relative to the anti form;  $f_g$  and  $f_a$  are the vibrational and rotational partition functions for the two conformers, however,  $f_g/f_a$  was neglected in the present calculations (see e.g. [2]).

taken from literature data (see e.g. CYVIN's book [6]) with the exception of l(S-C) which was estimated from the experimental radial distribution.

Refinement. The least squares method was applied to the molecular intensities in the form corresponding to Equation (1). The  $1.75 \le s \le 30.25$  Å<sup>-1</sup> data interval was utilized. A diagonal weight matrix was used. The refinement was carried out by iteration alternately fixing either the geometry and mean amplitudes of vibration or the amounts of the two forms, respectively. When refining the geometrical parameters, not all of them could be varied simultaneously. Thus different constraints were applied taking also into account correlation among parameters. The bond lengths, bond angles, the torsional angle and some of the mean amplitudes of vibration determined are presented in Table II. The  $\sigma_{LS}$  standard deviations shown were obtained by

	Parameters	$\sigma_{LS}$	σ
-(C H) Å	1 19	0.000	0.012
r(с—н), А	0.076	0.009	0.013
r(S-H), Å	1.40	0.02	0.028
u(S—H), Å	0.07	0.04	0.057
r(C-C), Å	1.53	0.02	0.028
<i>l</i> (C-C), Å	0.06	0.03	0.042
r(S-C), Å	1.819	0.002	0.006
l(S—C), Å	0.061	0.005	0.007
C—C—S	112.0°	0.9°	1.3°
S—С—Н	107.0°	2.2°	3.1°
С—Ѕ—Н	90.5°	3.2°	4.5°
$\tau(S-C-C-S)$	106.3°	3.5°	5.0°
l(S.C)	0.074	0.005	0.007
l(SS) gauche	0.15	0.02	0.028
l(S.S) anti	0.122	0.009	0.013

Ta	ь	le	T
1		10	**

the least squares procedure. In this all the geometrical parameters and mean amplitudes of vibration were allowed to vary with the exception of the following: mean amplitudes of vibration of the hydrogen-hydrogen distances for both forms and of the carbon-hydrogen distances for the gauche form. The standard deviations are relatively large and in calculating the  $\sigma_t$  total errors, also shown in Table II, the experimental error of about 0.2 per cent can be neglected in all cases but in that of the S-C bond distance. To take account of possible correlation among the observations, the values of  $\sigma_{LS}$  were multiplied by a
factor of  $\sqrt{2}$  in obtaining the values of  $\sigma_t$ . Justification for this has been given by HEDBERG and IWASAKI [7].

The least squares refinement for the amounts of the *anti* and *gauche* forms resulted in 62 and 38 per cent, respectively, with 3 per cent standard deviation. If multiplied by  $\sqrt{2}$  for the same reason as given above, 4.2 is obtained. This still seems to be, and probably is, too small partly because in calculating the  $\sigma_{LS}$  values for the amounts of conformers, the geometry of the forms was not allowed to vary.

The parameters of Table II were used in calculating the theoretical distributions T of Fig. 2, and A, G and 62% A + 38% G of Fig. 4.

### Discussion

No unusual values were obtained for the geometrical parameters. A detailed comparison with literature data would not be relevant because of the large uncertainties of the parameters obtained for ethane-1,2-dithiol. The possible exception is the S—C bond distance. For this bond  $1.802 \pm 0.002$  Å,  $1.8177 \pm 0.0002$  Å and  $1.814 \pm 0.003$  Å were obtained in CH<sub>3</sub>—S—CH<sub>3</sub> [8], CH<sub>3</sub>—S—H [9] and CH<sub>3</sub>S—C=CH [10], respectively.

The torsional angle found in ethane-1,2-dithiol is compared with those in other 1,2-disubstituted ethanes in Table III.

	F [11]	Cl [11, 12]	Br [11]	NH <sub>2</sub> [13]	SH, this work
more stable conformer	gauche	anti	anti	gauche	anti
anti form present	4—15%	$73\pm7\%$ [11] $73\pm5\%$ [12]	82—93%	may be a small fraction only	62±4.2%
gauche form from anti					
au torsional angle	110.6±7°	$\begin{array}{ccc} 116.0^{\circ} & [11] \\ 109 {\pm} 5^{\circ} & [12] \end{array}$	106.3°	116.0±5.0°	106±5°
temperature of					
the electron dif- fraction experi- ment	14 °C	—7 °C [11] 22 °C [12]	22 °C	55—118 °C	70 °C

#### Table III

Data on 1,2-disubstituted ethanes

The mean amplitudes of vibration of the bonds as well as of the S.C. distance shown in Table II are normal. The values for l(S...S), both gauche and anti, are quite large. This may be an indication of strong torsional motion.

The relative abundance of the conformers found in ethane-1,2-dithiol is close to that determined for dichloro-1.2-ethane. There is a marked tendency of the amount of the gauche form to decrease with increasing mass of the substituent as shown by the data in Table III.

The energy difference between the anti and gauche forms of ethane-1,2--dithiol calculated from their relative abundance according to Eq. (2) is 0.8 kcal/mol. This value is in reasonably good agreement with the spectroscopic results.

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# A SIMPLE METHOD FOR THE DETERMINATION OF THE RATE OF CORROSION

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A modified technique is described for the electrochemical evaluation of the rate of corrosion, based on the determination of the polarization resistance. The method consists in measuring the resistance of a cell containing two identical electrodes. The polarization resistance can be determined if the resistance of the electrolyte is known. The new method is especially suitable for corrosion studies in organic solvents, as well as lacquers, paints and melts, as the necessity to use a reference electrode is eliminated.

The method of 'linear polarization' or, more exactly, 'polarization resistance' is widely used for the determination of the corrosion rate of metals according to WAGNER and TRAUD [1] and STERN and GEARY [2]. The method consists essentially in the measurement of the polarization resistance of metal electrodes immersed in the corrosive medium. The polarization resistance is given by

$$R_p = \left(\frac{dE}{di}\right)_{i=0} \tag{1}$$

(where E is the electrode potential, i is the current density). If the rates of metal oxidation and reduction of the oxidized component are controlled by a charge-transfer reaction,\*\* the equation of the polarization curve can be written in the following form:

$$i = i_c \left( e^{\frac{E-E_c}{b_a}} - e^{\frac{E-E_c}{b_k}} \right), \tag{2}$$

where  $E_c$  is the corrosion potential and  $i_c$  is the corrosion current density;  $b_a$  and  $b_k$  are the Tafel slopes for the anode and cathode processes, respectively. The slope of the polarization curve at the corrosion potential  $E_c$  is

$$\left(\frac{di}{dE}\right)_{E_c} = \frac{1}{\left(\frac{dE}{di}\right)_{i=0}} = \frac{1}{R_p} = i_c \left(\frac{1}{b_a} + \frac{1}{b_k}\right),\tag{3}$$

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\*\* The method can be extended to other kinds of polarizations, too (cf. H. KAESCHE: Die Korrosion der Metalle, Springer Verlag, Berlin 1966).

Hence, the corrosion current density is given by

$$i_c = \frac{1}{R_p} \frac{b_a b_k}{b_a + b_k}$$
 (4)

The polarization resistance  $(R_p)$  can be determined by graphical differentiation of the polarization curve at i = 0, thus the polarization curve has to be determined only in the neighbourhood  $(E_c = \pm 5 \text{mV})$  of the corrosion poteniial. The measurement of parameters  $b_a$  and  $b_k$ , which are inaccurate because of the inhomogeneity of the metal surface, can be omitted. Thus sufficient accuracy ts attained by employing the Tafel constants evaluated by the formula

$$b = \frac{RT}{\alpha z F} \tag{5}$$

assuming  $\alpha \approx 0.5$  (*R* is the universal gas constant,  $\alpha$  — the transfer coefficient, *T* — the absolute temperature, *z* — the number of electrons involved in the electrode reaction, *F* — the Faraday constant).

The above method permits rapid and simple evaluation of the rate of corrosion. However, the choice of the reference electrode is difficult in some cases such as the investigation of corrosion in organic solvents, lacquers, paints and melts. We have developed a technique to overcome this difficulty by dispensing with the use of a reference electrode.

The method is based on the following considerations: the determination of corrosion current density does not require the knowledge of the polarization curve of the electrode as measured by conventional methods but only that of the polarization resistance. The latter can be determined from the current-potential curve of a measuring cell containing two identical electrodes. The cell voltage or the current-potential curve of a cell consisting of two electrodes made of the same material with identical surface areas A, is given, in the case of uniform current density distribution i on the electrodes polarized by current I, by the formula:

$$U(i) = E_1(i) - E_2(-i) = IR = E_1(i) - E_2(-i) + iAR,$$
(6)

where  $E_1$  and  $E_2$  are the potentials of the anodically and cathodically polarized electrodes, respectively, and R is the resistance of the solution between the two electrodes.

The derivative of Eq. (6) at i = 0 is

$$\left(\frac{dU}{di}\right)_{i=0} = \left(\frac{dE_1}{di}\right)_{i=0} + \left(\frac{dE_2}{di}\right)_{i=0} + AR.$$
(7)

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However

$$\left(\frac{dE_1}{di}\right)_{i=0} = \left(\frac{dE_2}{di}\right)_{i=0} = \left(\frac{dE}{di}\right)_{i=0},\tag{8}$$

as the slope of the polarization curve is independent of the direction from which the current-potential curve at zero is approached. Thus by using Eqs (1), (7) and (8) one obtains

$$\left(\frac{dU}{di}\right)_{i=0} = 2\left(\frac{dE}{di}\right)_{i=0} + AR = 2R_p + AR, \qquad (9)$$

whence the polarization resistance is

$$R_{p} = \frac{\left(\frac{dU}{di}\right)_{i=0} - AR}{2} \tag{10}$$

 $\left(\frac{dU}{di}\right)_{i=0}$  can be obtained by graphical differentiation of the current-potential curve of the measuring cell and R can be determined by an A.C. method (e.g. an A.C. bridge).

### Notes

(1) It is advisable to place the electrodes in parallel at a distance from one another which is smaller than the linear dimensions of the electrodes, to ensure uniform current density distribution. The rear plates of the electrodes should be covered by an insulating layer preventing the contact of the surface and the medium.

(2) The electromotive force of the measuring cell may differ from zero even at i = 0 because of the inhomogeneity of the metal surfaces. This phenomenon does not impede the determination of the polarization resistance as Eq. (6) is only augmented by a constant  $U_0$  in this case and the derivative of the latter is  $dU_0/di = 0$ .

(3) The polarization resistance of the cathode and anode may not be identical because of the inhomogeneity of the electrode surfaces, *i.e.*  $R'_p \neq R''_p$  and Eq. (8) is not valid. In such cases Eqs (9) and (10) have the following form:

$$\left(\frac{dU}{di}\right)_{i=0} = R'_p + R''_p + AR, \qquad (9a)$$

$$R_{p} = rac{R'_{p} + R''_{p}}{2} = rac{\left(rac{dU}{di}
ight)_{i=0}}{2} - AR$$
 (10a)

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thus the right-hand side of Eq. (10) is equal to the arithmetical mean of the two polarization resistances. In such cases simultaneous measurements are made on two samples and consequently the number of parallel tests can be decreased by one half.

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# INFRARED SPECTROSCOPIC INVESTIGATION OF MORPHINE DERIVATIVES, I

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### Received March 8, 1971

The infrared spectra of codeine (IA), dihydrocodeine (IIA) and their derivatives were studied in order to examine the applicability of this method for the elucidation of structural and steric structural problems in ring C.

It was found that

— the saturated or unsaturated character of ring C can be established unambiguously on the basis of the infrared spectra;

biguously on the basis of the infrared spectra; — in  $C_6$ —X and  $C_8$ —X substituted unsaturated compounds characteristic differences appear in the 800—1000 cm<sup>-1</sup> region. Here bands of high intensity — denoted by "E" — appear in the case of a closed ring E; substituents  $C_6$ —X and  $C_8$ —X give rise to bands in the 940±10 cm<sup>-1</sup> and 900±13 cm<sup>-1</sup> regions, respectively; — the characteristic bands of the  $C_6$ —X substituents appear in the compounds

— the characteristic bands of the  $C_6$ —X substituents appear in the compounds examined in accordance with the supposed configurations, and in agreement with the general statements of the literature;

— on the basis of the results obtained with compounds containing saturated ring C and axial  $C_6$ —X substituents, in these derivatives a conformational equilibrium is supposed between molecules containing ring C in chair and flexible boat conformations.

The aim of the present work was to examine the utility of infrared spectroscopy, the elucidation of the structural and steric structural problems of codeine, dihydrocodeine and their derivatives. The present investigations have been focussed primarily on ring C.

These problems have been studied by several researchers by means of chemical [1a,b,c,d,e,f,g,h,i], as well as modern physical X-ray [2a,b,c] and NMR [3a,b] methods. The most probable steric structures of codeine (IA), morphine (IB), dihydrocodeine (IIA) and dihydromorphine (IIB), which are in the best agreement with the results of the above investigations can be given as follows:



Infrared spectroscopic studies on the steric structural problems of ring C of morphine derivatives have not been published yet; only the investigations of Rüll [4] on three codeine derivatives approached this field.

The following questions of detail have been investigated by us: the use of infrared spectroscopy in

(a) deciding the saturated or unsaturated character of ring C,

(b) the differentiation between the position of the substituent X located at  $C_6$  ( $\Delta^{7,8}$ ) or  $C_8$  ( $\Delta^{6,7}$ ).

(c) the determination of the steric arrangement of the  $C_6$ -X substituents in saturated and unsaturated compounds.

The compounds listed in Table I were used for these investigations; a new nomenclature was suggested for the substance [5]. The infrared spectra

Name		Configuration of substituent X	Ref.
Dihydrocodeinone	ш	$C_6 = 0$	6
Isocodeine	IV	$C_6 - OH$ (ax')	7
Dihydroisocodeine	V	$C_e - OH$ (eq)	7
8-Deoxy-8-thiol-pseudocodeine	VI	C <sub>8</sub> -SH (eq')	8
6-Deoxy-6-thiol-dihydroisocodeine	VII	C <sub>6</sub> -SH (eq)	8
Codeine-6-0-methylether	VIII	$C_6$ —OCH <sub>3</sub> (eq')	9
Tetrahydrothebaine	IX	$C_6 - OCH_3$ (ax)	9
6-Deoxy-6-chloroisocodeine	X	$C_6$ —Cl (ax')	6
6-Deoxy-6-fluoroisocodeine	XI	$C_6$ —F (ax')	10
6-Deoxy-6-chlorodihydroisocodeine	ХП	$C_6 - Cl (eq)$	6
Deoxycodeine-E	XIII	_	11
Dihydrodeoxycodeine D	XVI	_	12
Dihydrothebainone	XV	$C_{6} = 0$	9
6-0-Acetyldihydroisocodeine	XVI	$C_6 - OCOCH_3$ (eq)	7
6-0-Acetyldihydrocodeine	XVII	$C_6 - OCOCH_3(ax)$	6
3-0-Benzylmorphine	XVIII	C <sub>6</sub> -OH (eq')	6
Norcodeine	XIX	C <sub>6</sub> -OH (eq')	6
Isomorphine	XX	C <sub>6</sub> -OH (ax')	13
8-Desoxy-8-azidopseudocodeine	XXI	$C_8 - N_3$ (eq')	14
3-0-Acetyl-8-deoxy-8-azidopseudomorphine	XXII	$C_8 - N_3$ (eq')	14
8-Deoxy-8-aminopseudocodeine	XXIII	$C_8$ -NH <sub>2</sub> (eq')	14
8-Deoxy-8-chloropseudocodeine	XXIV	$C_8$ —Cl (eq')	6
8-Deoxy-8-bromopseudocodeine	XXV	C <sub>8</sub> -Br (eq')	12
8-Deoxy-8-iodopseudocodeine	XXVI	C <sub>8</sub> —I (eq')	6
8-Deoxy-8-isothiocyanopseudocodeine	XXVII	$C_8 - NCS$ (eq')	15

Table I

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of the compounds containing phenolic hydroxyl groups — except dihydrothebainone (**XV**) — were studied only in the 800—1000 cm<sup>-1</sup> wavenumber range, since the presence of a phenolic hydroxyl group makes the spectra very complicated.

### (a) Investigation of the saturated or unsaturated character of ring C

In the case of the compounds examined, the band of the C = C stretching vibration ( $\nu C = C$ ) cannot be utilized for the determination of the saturated or unsaturated character of ring C, since this is usually overlapped by a strong band appearing in the same region; this is due to the slightly deformed aromatic ring.

However, bands of medium intensity characteristic of the  $\nu$ (= CH) and  $\gamma$ (= CH) vibrations of *cis* ethylene double bonds could be found in the regions given in the literature [16] (Table II); these bands are missing in the spectra of the corresponding saturated analogues.

It should be noted, however, that on the basis of these bands (Table II) no unambiguous differentiation was possible between compounds containing  $\Delta^{6,7}$  or  $\Delta^{7,8}$  unsaturated bonds.

Compound	$\nu(=CH)$ cm <sup>-1</sup>	$\gamma (=C)$	H) 1 <sup>-1</sup>
IA	3020	687	709
IV	3028	680	718
VIII	3028	?	707
X	3029	687	710
XI	3023	690	720
XIII	3028	687	709
VI	3012	697	710
XIX	3010	693	722 ?
XX	3030	683	722
XXI	3024	682	705
XXII	3025	685	702
XXIII	3020	685	702
XXIV	3032	687	703
XXV	3031	690	?
XXVI	3029	683	701
XXVII	3031	?	704

**Table II** 

The saturated or unsaturated character of ring C is also indicated by the bands assigned to ring E (dihydrofuran ring). The great strain of the C<sub>4</sub>— —O—C<sub>5</sub> bond in the ring will deform ring A, and this effect is even more pronounced in ring C [3a].

On the basis of the literature [17], it can be stated that if the furan skeleton is attached to a rigid ring system, a band of v C — O character can be found in the 930—980 cm<sup>-1</sup> region. In addition to this, the spectrum has further characteristic absorption maxima between 1210—1260 cm<sup>-1</sup> and 985—1000 cm<sup>-1</sup>.

In the spectra of morphine derivatives, several characteristic bands can be found in the 880—1210 cm<sup>-1</sup> region; further on, these will be denoted as "E"-bands (Table III) which are missing in the absence of the  $C_4$ —O—C<sub>5</sub> bond.

T	a	h	le	T	П

Character of ring C			"E"-bands cm <sup>-1</sup>	,	
Unsaturated	910±10 m	940±10 vs	965 <u>+</u> 10 s	$1035{\pm}10~{ m vs}$	1200 m—w
Saturated	910±10 m—w	945 <u>+</u> 10 m	965±5 m	1010? 1040?	$1080 \pm 1 \text{ s}$ $1190 \pm 5 \text{ m}$

The intensities of the bands are indicated as usual in the literature: vs: very strong; s: strong; m: medium; w: weak.

If ring C has unsaturated character, these absorption have usually high intensities. They are due to complex group vibrations and can, in general, be considered characteristic of the strained dihydrobenzofuran ring system.

# (b) Determination of the position of substituent X at $C_6 \ \Delta^{7,8}$ or $C_8 \ \Delta^{6,7}$

Table IV lists the wavenumber values of the most intense maxima of the band groups usually appearing as triplets in the infrared spectra of the compounds (recorded in KBr pellets).

It can be seen that the substitution pattern ( $C_6$  or  $C_8$ ) of ring C can be determined unambiguously on the basis of the appearance of the "E"-bands in the 880–1000 cm<sup>-1</sup> region.

This observation can be well utilized in the structural investigations of the products formed in the nucleophilic substitution reactions of the 6-0-tosyl and 6-0-mesyl derivatives studied by us, thus indirectly facilitating the evaluation of the reaction mechanism [5].

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Compound Substituent		Band maximum, cm <sup>-1</sup>	Average cm <sup>-1</sup>	
IA	6—OH (eq')	936 s		
IV	6-OH (ax)'	942 s		
VIII	6-OCH <sub>3</sub> (eq)'	941 s		
X	6-Cl (ax)'	938 s	$940\pm10$	
XI	6-F (ax)'	945 vs		
XIX	6-OH (eq)'	950 s		
XX	6-0H (ax)'	930 s		
VI	8—SH	903 vs		
XXI	8—N <sub>3</sub>	913 vs		
XXII	8—N <sub>3</sub>	913 vs		
XXIII	8—NH <sub>2</sub> (eq')	887 s		
XXIV	8—Cl	901 s	900±13	
XXV	8—Br	900 vs		
XXVI	8—I	895 vs		
XXVII	8-NCS	892 vs		

**Table IV** 

The values measured can be found within  $\pm 5 \text{ cm}^{-1}$  in the spectra recorded in chloroform solution.

### (c) Steric position of the $C_6-X$ substituents

Table V shows the wavenumber values of the  $C_6$ —X and X—H stretching vibrations of the  $C_6$ —X ( $\Delta^{7,8}$ ) unsaturated derivatives.

It can be seen that the characteristic vibrational frequency values of the  $C_6$ —X substituents correspond to the supposed steric positions, in accordance with the general statements given in the literature [18,a,b,c] (Table I). The dissimilar positions of the  $C_6$ —OH groups in codeine (IA) and isocodeine (IV) clearly appear in the 3000—3700 cm<sup>-1</sup> regions of the spectra (Fig. 1).

It can be seen that in the spectra recorded in KBr pellets a sharp intense band (3520 cm<sup>-1</sup>) and a broad absorption maximum (3150 cm<sup>-1</sup>) appear in the case of codeine and isocodeine, respectively (Fig. 1A). In the spectra recorded in chloroform solution (Fig. 1B) the characteristic bands are found at 3580 cm<sup>-1</sup> (IA) and 3610 cm<sup>-1</sup> (IV). On dilution, the band of codeine (IA) found at 3580 cm<sup>-1</sup> shows only small changes within the limit of error, while in the case of isocodeine (IV) an intensity variation can be observed: the intensity of the maximum at 3150 cm<sup>-1</sup> decreases, while that appearing at 3610 cm<sup>-1</sup> shows increased intensity. In order to explain these phenomena starting with the known configuration of the C<sub>6</sub>—OH groups — the formation of a weak intramolecular hydrogen bridge can be assumed in the solid state

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Fig. 1. OH stretching vibration bands of codeine (\_\_\_\_\_) and isocodeine (\_\_\_\_\_) in spectra recorded in KBr pellets (A) and CHCl<sub>3</sub> solutions (B)

Compound	Substituent	Steric	$\nu(C_6 - cm^{-1})$	-X)	$\nu(X-H)$ cm <sup>-1</sup>	
		position	CHCl <sub>3</sub>	KBr	CHCl <sub>3</sub>	KBr
Codeine (IA)	ОН	(eq')	1060 (1050)+	1060	3560 (3549)+ 3350	3520 3460
Isocodeine (IV)	ОН	(ax')	1024	1022	(3665)+ 3610 3370	3150
Codeine-6-0-methyl-ether (VIII)	OCH <sub>3</sub>	(eq')	1125	1120	3150	
a-Chloro-codide (X)	Cl	(ax')		761 808?		
α-Fluorocodide (XI)	F	(ax')	1155	1152		

Table
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\* The data of RÜLL [4] are given in brackets.

between the quasi-equatorial OH (eq') group and the ethereal oxygen atom of ring E in the case of codeine (IA), while the quasi-axial (ax') OH group of isocodeine (IV) can participate in a stronger intermolecular hydrogen bond.

In the chloroform solution spectra, however, the presence of solventsolute associates of various stability should be assumed. This is probably also responsible for the different positions of the  $3610 \text{ cm}^{-1}$  and  $3580 \text{ cm}^{-1}$  bands, in addition to the appearance of bands of low intensity between  $3200 \text{ cm}^{-1}$ 

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and 3500 cm<sup>-1</sup>. Namely, the two OH groups cannot be considered chemically equivalent, thus bond strength of the associates formed with the solvent may also be different. (Carbon tetrachloride is not a suitable solvent because of the poor solubility of a considerable number of these compounds.) It should be noted that in isocodeine (IV) the existence of a probably very weak intramolecular hydrogen bond between the C<sub>6</sub>—OH (ax') group and the  $\Delta^{7.8}$  double bond cannot be excluded, but this could not be confirmed unambiguously.

Ring C in the  $\triangle^{7,8}$ -unsaturated compounds has a flat boat conformation, while in the saturated derivatives it has a chair conformation which is slightly distorted because of the C<sub>4</sub>—O—C<sub>5</sub> bond [3a, 4]. Thus, in the dihydro derivatives the configuration of the C<sub>6</sub>—X substituent is changed as compared with the corresponding unsaturated derivatives. This configurational change is also revealed by the wavenumber values of the characteristic vibrations of the bonds in question. The wavenumbers characteristic of the C<sub>6</sub>—X bonds in the saturated derivatives are listed in Table VI.

Compound	Substituent	Steric	$\nu(C_6-X)$ cm <sup>-1</sup>		v(X-H) cm <sup>1</sup>	
		position	CHCl <sub>3</sub>	KBr	CHCl <sub>3</sub>	KBr
Dihydrocodeine ( <b>IIA</b> )	ОН	ax	1044 (1035)* 1079	1050	3590 (3645)* (3580)* 3565 3380 3160	3127
Dihydroisocodeine (V)	ОН	eq	1042 (1038)*	1048 3648	3605 (3648)* (3586)* 3415 3150	3130
6-Deoxy-6-thiol-dihydroisocodeine (VII)	SH	eq	640	642	2500 broad	2549
Tetrahydrothebaine (IX)	OCH3	ax	1120 1109 broad 1098	1097		
Dihydro-a-chlorocodide (XII)	Cl	eq		751		

**Table VI** 

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Compound	Substituent	Steric posi- tion	$v \stackrel{C=0}{\operatorname{cm}^{-1}}$		<i>vas</i> C-0-C cm <sup>-1</sup>		$\delta_s CH_3 \ cm^{-1}$	
			CCl,	KBr	CCl,	KBr	CCl,	KBr
6-0-Acetyl-dihydrocodeine	CH <sub>3</sub> COO	ax	1748	1738	1245	1248	1379	
(XVII)		1.1.1	broad				br	1380
					1225	1225	1365	1374
			1.4.3		1205	1195	A State State	1363
					1190			
6-0-Acetyl-dihydroisocodeine (XVI)	CH <sub>3</sub> COO	eq	1743	1740	1240 broad	1240	1380	1875
					1200	the states	1362	1365

Table VI (continued)

### \* Data by RÜLL [4]

The wavenumber values observed, in accordance with the literature data [18a, b, c], are in agreement with the supposed steric positions. Similarly to the case of the unsaturated compounds, it can be stated that the configuration of the  $C_6$ —X group usually alters the wavenumber values of the  $\nu C_6$ —X band only slightly.

The  $\nu O$ —H regions of the epimeric pair containing C<sub>6</sub>—OH group, dihydrocodeine (IIA) and dihydroisocodeine (V), are shown in Fig. 2.

It is surprising that the spectra recorded in KBr pellets (Fig. 2A) show almost no difference. This indicates that in both compounds the  $C_6$ —OH groups participate in stable hydrogen bands. Significant differences appear, however, in the 3500—3650 cm<sup>-1</sup> regions of the solution spectra. Dihydroisocodeine (V) gives one band at 3603 cm<sup>-1</sup>, while dihydrocodeine (IIA)



Fig. 2. OH stretching vibration bands of dihydrocodeine (\_\_\_\_\_) and dihydroisocodeine (\_\_\_\_\_) in spectra recorded in KBr pellets (A) and  $CHCl_3$  solutions (B)

absorbs at 3590 cm<sup>-1</sup> and 3565 cm<sup>-1</sup>. The different positions of the bands found at 3590 cm<sup>-1</sup> and 3603 cm<sup>-1</sup> can be explained by the existence of a hydrogen bond between the  $C_6$ —OH group and the ethereal oxygen atom of ring E. In dihydrocodeine (IIA) the  $C_6$ —OH group is in axial position, and this configuration may give rise to a stronger hydrogen bridge with the ethereal oxygen atom of ring E, since the two pillar atoms of the hydrogen bridge are nearer to each other than in dihydroisocodeine (where  $C_6$ —OH is in equatorial position).



Fig. 3. OH stretching vibration bands of dihydrocodeine

In order to elucidate whether the band positions observed in chloroform solutions, as well as the shoulder appearing at  $3565 \text{ cm}^{-1}$  in the case of dihydrocodeine are due to associates formed with the solvent molecules which have different strengths because of the different steric positions, dihydrocodeine (**IIA**) was also examined in an apolar solvent (CCl<sub>4</sub>); the corresponding part of the spectrum is shown in Fig. 3.

It can be seen that in carbon tetrachloride solution — as compared with the chloroform solution of identical concentration — a frequency increase of 10 cm<sup>-1</sup> occurs, which confirms the existence of associates with chloroform. On the effect of dilution (Fig. 3), however, a further — although small, about 5—6 cm<sup>-1</sup> — wavenumber shift occours, which is probably due to the rupture of the weak intramolecular hydrogen bridge formed with the ethereal oxygen atom of ring E. Still, the shoulder characteristic of dihydrocodeine (IIA) which is shifted to higher wavenumber values as a result of the decreased polarity of the solvent and dilution, appears in each case. In general it can also be observed in other regions of the spectra (Table VI) that in the presence of *axial* C<sub>6</sub>—X groups, characteristic band splittings of "shoulder" appear as compared with the corresponding equatorial compounds.

In order to explain these phenomena, on the basis of the literature dealing primarily with steroids [18b, 19a, b, c, d] it can be supposed that the dihydro compounds containing axial  $C_6$ —X groups are present in a shifted conformer equilibrium in solutions. This conformer equilibrium may exist

between form a characterized by the chair conformation of ring C and form c of 'flexible boat' conformation (which is strongly shifted toward a); the so-called "classical boat" conformation b of ring C cannot develop because of energetical reasons (Fig. 4). This assumption is confirmed by an inspection of the Dreiding model. Detailed theoretical and temperature-dependent infrared and NMR studies of this problem are in progress.



a)



b)



c)

Fig. 4. Supposed conformational limiting cases of ring C in dihydro-  $(C_6 - X ax)$  derivatives: (a) chair; (b) classical boat; (c) flexible boat

### Experimental

The infrared spectra were recorded with a Zeiss UR-10 spectrophotometer. The wavenumber calibration of the instrument was checked by recording the spectrum of a polystyrene foil  $(d = 0.25 \mu)$ . The accuracy of the wavenumber values given is  $\pm 2 \text{ cm}^{-1}$ . The spectra were recorded in solid state (KBr pellets) and in chloroform (in some cases, in carbon tetrachloride solutions). Unfortunately, the general use of carbon tetrachloride as a solvent, which would have been more advantageous from several points of view, was not possible because of the poor solubility of a significant number of the compounds examined.

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# REACTIONS OF OSMIUM COMPOUNDS WITH AMINO ACIDS

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### Received December 6, 1971

The oxidative effect of  $OsO_4$  and  $K_2OsO_4$  on amino acids has been investigated in 0.5 N sodium hydroxide at 100 °C. It has been established that, with the exception of proline, oxyproline,  $\beta$ -alanine and  $\gamma$ -aminobutyric acid, the quantity of ammonia liberated in the reaction with osmium tetroxide is twice greater than that with potassium osmate. Both osmium compounds are reduced to osmium dioxide in the course of the reaction.

A detailed study of the desamination reaction of glycine and  $\alpha$ -alanine shows that in the first case glycalic acid is formed besides ammonia, which, however, is immediately oxidized to oxalic acid. The oxidation product of  $\alpha$ -alanine is, in addition to ammonia, pyruvic acid. The further oxidation of the latter to carbon dioxide and acetic acid is a slow process. On the basis of the results obtained so far, it is assumed that ammonia and

On the basis of the results obtained so far, it is assumed that ammonia and the corresponding ketonic acid are formed from the various amino acids by the action of  $OsO_4$  or  $K_2OsO_4$ . The extent of ammonia liberation depends decisively on the ratio of the rate of ammonia and ketonic acid formation and the rate of the subsequent oxidation of the ketonic acid.

The desaminating effect of osmium tetroxide and potassium osmate on various amino acids has been investigated. The  $OsO_4$  used was a p.a. Merck preparation, while  $K_2OsO_4$  has been prepared in our laboratory by the reduction of osmium tetroxide with ethyl alcohol in alkaline medium [1], and purified by repeated recrystallization. The osmium content of the stock solutions was checked by spectrophotometry [2]; the nitrogen content of the amino acids, manufactured by Merck and la Roche, was determined by the micro-Kjeldahl method. Desamination measurements were carried out in a 0.5 molar sodium hydroxide medium at 100 °C. High purity nitrogen was passed through 7.5 ml volumes of solutions,  $4 \times 10^{-3}$  molar in osmium and  $4 \times 10^{-2}$  m olar in the acid, and the amount of ammonia liberated was measured by titration against N/70 sulfuric acid [3].

The quantities of ammonia liberated by  $OsO_4$  and  $K_2OsO_4$ , respectively, are shown in Tables I and II.

On the basis of these data, the following can be established.

The quantity of ammonia formed during the reaction of osmium compounds with amino acids attains with most of the amino acids a limiting value within the time of investigation. With the exception of proline and oxyproline, which do not contain  $NH_2$  groups, and of  $\beta$ -alanine and  $\gamma$ -aminobutyric acid, the amount of ammonia liberated in the reaction with osmium tetroxide is twice the amount of that liberated by potassium osmate.

After the desamination reactions,  $OsO_2$  is present in the reaction mixtures in the form of a black precipitate [4].

Contrary to our earlier observations concerning the reaction of ethylenediamine with osmium tetroxide [3], the nitrogen content of systems containing amino acids can be determined quantitatively by the Kjeldahl method after desamination with no nitrogen deficiency being observed.

In our further studies, the reactions of glycine and  $\alpha$ -alanine with osmium compounds have been investigated more extensively, in view of the fact

	10	30	60 min
Glycine	2.8×10 <sup>-3</sup>	3.7×10 <sup>-3</sup>	3.9×10 <sup>-3</sup> molNH <sub>3</sub>
α-Alanine	7.4	7.9	7.9
Valine	4.0	5.2	6.0
Leucine	4.8	5.9	6.1
Isoleucine	5.0	6.0	6.2
Norleucine	5.7	5.8	6.0
Methionine	2.0	3.0	3.0
Serine	3.3	4.9	5.4
Threonine	3.1	5.4	6.8
Aspartic acid	3.8	5.3	6.0
Glutamic acid	5.1	6.0	6.2
C-phenylglycine	3.9	5.5	6.0
Phenylalanine	4.9	6.0	6.2
Tyrosine	4.1	5.9	6.1
Proline	0.7	0.9	0.9
Oxyproline	0.8	1.0	1.0
Tryptophan	3.9	5.3	5.1
Histidine	2.1	3.4	4.0
Lysine	5.0	5.9	6.1
Arginine	2.8	5.0	7.0
Ornithine	3.2	5.8	7.1
Citrulline	6.0	6.0	6.2
$\beta$ -Alanine	3.4	3.9	3.9
γ-Aminobutyric acid	4.3	5.8	6.0

Table I

 $4 \times 10^{-3}$  mol  $OsO_4 - 4 \times 10^{-2}$  mol amino acid - 0.5 N NaOH, 100 °C

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### Table II

 $4 \times 10^{-3}$  mol  $K_2 OsO_4 - 4 \times 10^{-2}$  mol amino acid - 0.5 N NaOH, 100 °C

	10	30	60 min
Glycine	$1.2 \times 15^{-3}$	$1.8  imes 10^{-3}$	1.9×10 <sup>-3</sup> mol NH <sub>3</sub>
α-Alanine	3.6	4.0	4.0
Valine	2.4	2.9	2.9
Leucine	2.0	2.9	3.0
Isoleucine	2.2	3.0	3.1
Norleucine	2.1	2.9	3.0
Methionine	1.2	1.5	1.5
Serine	1.3	2.2	2.8
Threonine	1.2	2.8	3.8
Aspartic acid	2.2	2.7	3.0
Glutamic acid	2.3	3.1	3.2
C-phenylglycine	1.9	2.9	3.0
Phenylalanine	2.4	3.3	3.6
Tyrosine	1.3	2.3	2.9
Proline	0.7	0.9	0.9
Oxyproline	0.6	0.8	0.8
Tryptophan	1.8	3.0	3.3
Histidine	1.1	1.8	2.0
Lysine	2.6	3.2	3.2
Arginine	0.7	2.3	3.9
Ornithine	1.4	2.8	3.6
Citrulline	2.5	3.1	3.2
$\beta$ -Alanine	2.0	3.3	3.8
y-Aminobutyric acid	3.4	3.9	3.9

that at identical mole ratios half as much ammonia is liberated from glycine than from  $\alpha$ -alanine.

In the reaction of glycine with osmium tetroxide, simultaneously with the liberation of ammonia, also glyoxalic acid is formed:

$$CH_{2}(NH_{2})$$
— $COOH + OsO_{4} + 2 OH^{-} = NH_{3} + CHO$ — $COOH + OsO_{4}^{2-} + H_{2}O$ 

However, glyoxalic acid is not converted by the Cannizarro reaction into oxalic acid and glycolic acid, but is transformed completely to oxalic acid by osmate, formed as intermediate in the reduction of  $OsO_4$ :

$$CHO - COOH + OsO_4^{2-} + H_2O = COOH - COOH + OsO_2 + 2 OH^{-}.$$

Similar reactions occur when glycine is treated with potassium osmate:

$$\begin{array}{l} \mathrm{CH}_2(\mathrm{NH}_2)\mathrm{-COOH}+2\ \mathrm{OsO}_4^{2-}\mathrm{+}\ 2\ \mathrm{H}_2\mathrm{O}=\mathrm{NH}_3\mathrm{+}\\ \mathrm{+\ COOH}-\mathrm{COOH}\ \mathrm{+}\ 2\ \mathrm{OsO}_2\mathrm{+}\ 4\ \mathrm{OH}^-\end{array}$$

On the determination of oxalic acid, osmium dioxide was first removed from the mixture after acidification with acetic acid, then oxalic acid was precipitated with calcium acetate. The calcium oxalate precipitate was titrated in acetic acid medium with 0.02  $N \text{ KMnO}_4$ . In view of earlier observations concerning the glycine-glyoxalic acid system [5], no large excess of glycine was used in these investigations.

Data on the formation of oxalic acid are summarized in Table III. The same table contains also the quantities of oxalic acid formed from glyoxalic acid by Cannizarro reaction, or by the oxidative action of various osmium compounds.

### **Table III**

	10	30	60 min	
4×10 <sup>− 3</sup> mol OsO <sub>4</sub> 8×10 <sup>− 3</sup> mol glycine	2.3×10 <sup>-3</sup>	3.4×10-3	3.8×10 <sup>-3</sup> mol oxalic acid	
4×10 <sup>-3</sup> mol K <sub>2</sub> OsO <sub>4</sub> 8×10 <sup>-3</sup> mol glycine	1.0×10 <sup>-3</sup>	1.7×10-3	1.8×10-3	
$4  imes 10^{-3}$ mol glyoxalic acid	1.1×10 <sup>-3</sup>	$1.8 \times 10^{-3}$	1.9×10 <sup>-3</sup>	
$4 \times 10^{-3} \operatorname{mol} \operatorname{OsO}_4$				
$4  imes 10^{-3}$ mol glyoxalic acid	$3.4  imes 10^{-3}$	$4.1 \times 10^{-3}$	$4.1  imes 10^{-3}$	
$4 \times 10^{-3} \operatorname{mol} \mathrm{K_2OsO_4}$				
$4  imes 10^{-3}$ mol glyoxalic acid	3.3×10 <sup>-3</sup>	3.9×10 <sup>-3</sup>	4.0×10 <sup>-3</sup>	

Formation of oxalic acid from glycine and from glyoxalic acid (0.5 N NaOH, 100 °C)

As can be seen from the experimental data reported, the oxidation of glyoxalic acid to oxalic acid by the osmium compounds proceeds at a substantially higher rate than its disproportionation in an osmium-free alkaline medium. This can be attributed to the fact that in the reaction of glycine with osmium tetroxide or potassium osmate, osmium in the +8 or +6 oxidation state is reduced also in reactions not related to ammonia evolution.

The analogous reactions of  $\alpha$ -alanine with osmium tetroxide or potassium osmate are represented by the following equations:

$$\begin{array}{c} {\rm CH_3-CH(NH_2)-COOH\,+\,OsO_4+\,2\,OH^-\,=\,NH_3+\,CH_3-}\\ {\rm -\,CO\,-\,COOH\,+\,OsO_4^{2-}+\,H_2O;}\\ {\rm CH_3-CH(NH_2)-COOH\,+\,OsO_4^{2-}+\,H_2O\,=\,NH_3+\,CH_3-CO\,-}\\ {\rm -\,COOH\,+\,OsO_2+\,2\,OH^-} \end{array}$$

The presence of pyruvic acid has been established by chromatographic analysis [6].

The oxidation of pyruvic acid is known to lead to acetic acid and carbon dioxide. Therefore, it was investigated whether carbon dioxide is formed, and if so, at what rate and to what extent, when pyruvic acid is subjected to the action of osmium compounds at 100 °C in 0.5 N alkali. The analytical results [7] are shown in Table IV.

### **Table IV**

Formation of carbon dioxide from pyruvic acid (0.5 N NaOH, 100 °C)

	10	30	60 min
$4 \times 10^{-3} \text{ mol OsO}_4$			
8×10 <sup>-3</sup> mol pyruvic acid	$1.1  imes 10^{-3}$	3.4×10 <sup>-3</sup>	6.6×10 <sup>-3</sup> mol CO <sub>2</sub>
4×10 <sup>-3</sup> mol K <sub>2</sub> OsO <sub>4</sub>			
8×10 <sup>-3</sup> mol pyruvic acid	$0.7  imes 10^{-3}$	2.5×10 <sup>-3</sup>	5.0×10 <sup>-3</sup>

According to our investigations, no carbon dioxide is formed during the reaction of  $\alpha$ -alanine with osmium tetroxide or with potassium osmate.

On the basis of these experimental findings, the higher degree of desamination of  $\alpha$ -alanine, as compared to that of glycine, can be attributed to the fact that the oxidation of pyruvic acid formed in the desamination of alanine is much slower than the desamination. Owing to this, osmium in the +8 or +6 oxidation state is reduced by  $\alpha$ -alanine to an oxidation state of +4 only by reactions in which ammonia is liberated.

It may be assumed by the generalization of our observation on the desamination of  $\alpha$ -alanine and glycine that ammonia and the corresponding ketonic acid are formed from amino acids by the action of  $OsO_4$  or  $K_2OsO_4$ . The extent of ammonia liberation depends on the oxidation rate of the ketonic acid formed, relative to the desamination rate.

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# AUFBAU DES DIHYDROSHIKIMISÄURE- UND DES EPIDIHYDROSHIKIMISÄURE-TRIMETHYLÄTHERS AUS D-ARABINOSE

### EINIGE NEUE UMSETZUNGSPRODUKTE DER D-ARABINOSE V. MITTEILUNG\*

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Es wird die Synthese des Dihydroshikimisäure-trimethyläthers (IVa) und des Epidihydroshikimisäure-trimethyläthers (Va) bzw. ihrer Methylester (IVb und Vb) beschrieben. Die Ausgangssubstanz bildet der aus D-Arabinose zugängliche 2.3.4-D-arabo-Trimethoxy-5-tosyloxy-pentyl-cyanessigsäure-methylester (IIa) bzw. das analoge Malonester-Derivat (IIb). Beide Verbindungen können durch einen mit Natriummethylat bewirkten Ringschluß zu den entsprechenden Cyclohexan-Derivaten IIIa bzw. IIIb umgewandelt werden, die bei der Verseifung das gleiche Produkt, die (3R : 4S : 5R)-3.4.5-Trimethoxy-cyclohexan-1.1-Dicarbonsäure (IIIc) liefern. Die thermische, partielle Decarboxylierung dieser Dicarbonsäure führt zu einem Gemisch des Dihydroshikimisäure-trimethyläthers (IVa) und des Epidihydroshikimisäure-trimethyläthers (Va). Die Methylester IVb und Vb der diastereomeren Carbonsäure lassen sich voneinander chromatographisch trennen.

Das Scheitern unserer Versuche, eine Synthese der Chinasäure bzw. der Shikimisäure durchzuführen, deren entscheidender Schritt der Perkinsche Ringschluß eines entsprechenden, aus D-Arabinose zugänglichen 1.5-Didesoxy-1.5-dihalogen-D-arabit-Derivates darstellen sollte [1, 2], hat uns dazu bewogen, einen anderen, ebenfalls aus D-Arabinose ausgehenden Weg einzuschlagen. Nun haben vor kurzem BESTMANN und HEID [3] über eine sehr interessante Synthese der Chinasäure und der Shikimisäure berichtet, deren Ausgangssubstanz ebenfalls die D-Arabinose bildete. Dies veranlaßt uns, unseren Snytheseweg, der zum Trimethyläther der Dihydroshikimisäure (IVa) und der Epidihydroshikimisäure (Va) führte, bekannt zu geben, auch schon deshalb, weil durch die schöne Synthese der genannten Forscher das ursprünglich auch von uns angestrebte Ziel schon erreicht worden ist und wir die Fortsetzung unserer Untersuchungen nicht mehr beabsichtigen.

In einer unserer früheren Mitteilungen [4] haben wir über den Aufbau von 2.3.4-D-arabo-Trimethoxy-5-hydroxy-pentyl-cyanessigsäure (Ia) und des analogen Malonsäure-Derivats (Ib) berichtet. Die mit Hilfe von Diazomethan aus diesen Säuren gewonnenen Methylester Ic und Id wurden jetzt mit Tosylchlorid auf übliche Art zu den entsprechenden Tosylaten IIa und IIb umge-

<sup>\*</sup> IV. Mitteilung: Ann. Univ. Sci. Budapest, Sectio Chimica 13 (1972) im Druck. S. auch die vorläufige Mitteilung: Császár, J., BRUCKNER, V.: Acta Chim. Acad. Sci. Hung. 50, 405 (1966).

setzt, die sich dann durch Einwirkung von Natriummethylat unter Abspaltung der Tosyloxygruppe zu den entsprechenden Cyclohexan-Derivaten IIIa und IIIb cyclisieren ließen. Nach CAHN, INGOLD und PRELOG [5] ist die Verbindung IIIa als (3R:4S:5R)-1-Cyan-3.4.5-trimethoxy-cyclohexan-carbonsäuremethylester, die Verbindung IIIb als (3R:4S:5R)-3.4.5-Trimethoxy-cyclohexan-1.1-dicarbonsäure-dimethylester zu bezeichnen. Die Konfiguration des die Cyan- und Carbomethoxygruppe tragenden Asymmetriezentrums in Verbindung IIIa haben wir nicht bestimmt. Beide Ester lieferten bei der alkalischen Verseifung die (3R:4S:5R)-3.4.5-Trimethoxy-cyclohexan-1.1-dicarbonsäure (IIIc), die — in Gegensatz zu den öligen Estern IIIa und IIIb — als kristalline Substanz anfiel.



Wie zu erwarten war, erfolgte beim Schmelzen der 1.1-Dicarbonsäure IIIc eine partielle Decarboxylierung, die zur Bildung von den zwei diastereomeren Monocarbonsäuren IVa und Va führte. Die eine Komponente dieses Gemisches stellt den Trimethyläther der Dihydroshikimisäure (IVa), die andere den Trimethyläther der Epidihydroshikimisäure (Va) dar [6]. Dies ließ sich folgend beweisen: die durch Hydrierung der natürlichen (—)-Shikimisäure gewonnene Epidihydroshikimisäure [7] haben wir mit Hilfe von Diazomethan verestert, dann mit Dimethylsulfat veräthert; nun hat der gaschromatographische Vergleich dieses Produktes und des mit Hilfe von Diazomethan aus dem synthetisch zugänglichen Gemisch der diastereomeren Monocarbonsäuren

IVa und Va hergestellten Estergemisches (IVb + Vb) gezeigt, daß die eine Komponente des Estergemisches den Trimethyläther des Epidihydroshikimisäuremethylesters (Vb) darstellt (Abb. 1).

Das erhaltene Gaschromatogramm läßt zugleich darauf schließen, daß die partielle Decarboxylierung der Dicarbonsäure IIIc gewissermaßen stereo-



Abb. 1. Gaschromatographische Analyse des aus nativer (—)-Shikimisäure bzw. aus D-Arabinose hergestellten 3.4.5-Tri-O-methyl-dihydroshikimisäure-methylesters (Carbowax 20M/ Chromosorb Q; 200 °C). A) Aus nativer (—)-Shikimisäure gewonnenes Produkt (Vb); B) aus D-Arabinose gewonnenes Mischprodukt (IVb + Vb); C) gleichteiliges Gemisch von A) und B)



Abb. 2. ORD-Kurve des 3.4.5-Tri-O-methyl-dihydroshikimisäure-methylesters (IVb) und des 3.4.5-Tri-O-methyl-epidihydroshikimisäure-methylesters (Vb). Aufgenommen in Cyclohexan

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spezifisch verläuft, da im entstandenen Gemisch (IVa + Va) das Epidihydroshikimisäure-Derivat (Va) überwiegt (Abb. 1B). Das aus nativer (—)-Shikimisäure hergestellte Produkt stellt gleichfalls ein Gemisch von IVb und Vb dar, in welchem jedoch das Epidihydroshikimisäure-Derivat Vb sehr stark überwiegt (Abb. 1A). Aus diesem Befund folgt, daß entweder die katalytische Hydrierung der Shikimisäure nicht streng stereoselektiv verläuft, oder während der Methylierung des Epidihydroshikimisäure-methylesters eine geringfügige Inversion am Asymmetriezentrum 1 erfolgt.

Die diastereomeren Methylester IVb und Vb konnten durch Anwendung einer Silicagel-Säule chromatographisch getrennt werden. Ihre Elementaranalyse, der Verlauf ihrer ORD-Kurven (Abb. 2) und ihr IR-Spektrum weisen keine Differenzen auf, doch zeigen ihre NMR-Spektren deutlich den Unterschied ihrer Raumstrukturen.



Unter der Annahme, daß die Carbomethoxygruppe in beiden Verbindungen - wegen ihres größten Raumbedarfes - eine äquatoriale Lage einnimmt, müßte das in Stellung 4 in axialer Lage befindliche Proton der Verbindung IVb eine aa und ae Protonenwechselwirkung aufweisen. In der Tat stellt das Signal dieses Protons bei 3,18 ppm ein diesen Wechselwirkungen entsprechendes Dublett ( $I_{4,5} = 3$  cps;  $I_{4,3} = 9$  cps) dar. Die CH<sub>2</sub>-Gruppen zeigen im Gebiet der aliphatischen Protonen ein zusammenfließendes Bandenspektrum. Die Signale der Protonen, die den Methoxygruppen angehören, waren die folgenden: C4: 3,80 ppm, C3 und C5: 3,53 ppm, C1(COOCH3): 3,60 ppm. — Hingegen zeigt das NMR-Spektrum der Verbindung Vb folgendes: das Signal des in Stellung 4 in äquatorialer Lage befindlichen Protons erscheint — teilweise überlagert durch das Signal der Methoxy-Protonen bei 3,68 ppm, d.h. um einen Wert von 0,5 ppm höher als das axiale Proton in Position 4 der Verbindung IVb. Dies steht mit der allgemeinen Erfahrung in Einklang, daß Signale von Protonen in äquatorialer Lage höheren ppm Werten entsprechen. Das Signal des Protons in Stellung 1 der Verbindung Vb erscheint bei 2,60 ppm als teilweise zusammengeflossenes, jedoch gut deutbares Triplett, das der Kupplung mit den benachbarten beiden CH2-Gruppen entspricht ( $I_{ae} = 5$  cps;  $I_{aa} = 11$  cps). Die Signale der den Methoxygruppen angehörenden Protonen erscheinen bei den Werten  $C_4 = 3,78$  ppm,  $C_3$  und  $C_5 = 3,47$  ppm und  $C_1(COOCH_3) = 3,56$  ppm.

### Beschreibung der Versuche

#### Methodisches

Die Schmelzpunkte wurden im Tottoli-Apparat bestimmt und sind unkorrigiert. Die Siedepunkte der durch Vakuumdestillation gereinigten öligen Produkte beziehen sich auf die Temperatur des Ölbades der a. a. O. beschriebenen [2] Apparatur, die zur Kurzweg-Vakuumdestillation diente.

Die IR-Spektren wurden mit einem Doppelstrahlspektrofotometer vom Typ KR-10 der Fa. Carl Zeiss (Jena) in KBr-Tabletten aufgenommen.

Die NMR-Spektren wurden in einem Gerät vom Typ ZKR-60 der Fa. Carl Zeiss (Jena) in Deuterochloroform aufgenommen. Vergleichssubstanz: Tetramethylsilan.

#### 2.3.4-D-arabo-Trimethoxy-5-tosyloxy-pentyl-cyanessigsäure-methylester (IIa)

Eine auf 0° gekühlte und gerührte Lösung von 1,96 g 2.3.4-D-arabo-Trimethoxy-5hydroxy-pentyl-cyanessigsäure-methylester (Ie) [4] in 20 ml wasserfreiem Pyridin wurde portionsweise mit 1,62 g Tosylchlorid versetzt, nachher bei 0° noch 2 Stunden, danach bei Raumtemperatur weitere 5 Stunden gerührt. Nachdem das überschüssige Tosylchlorid durch Zusatz von 1 ml Wasser zersetzt worden ist, dampfte man die Lösung bei einer Badtemperatur von 40° i.V. ein. Die Lösung des öligen Rückstandes in 50 ml Äther wurde der Reihe nach mit n-Salzsäure, Wasser, 10% iger Kaliumhydrogencarbonat-Lösung und Wasser gewaschen, getrocknet (MgSO4), dann eingedampft und der ölige Rückstand bis zur Gewichtkonstanz in Vakuumexsiccator über konz. Schwefelsäure getrocknet. Der erhaltene hellbraune Sirup 

## 1750 cm<sup>-1</sup>; CH<sub>3</sub>O: 2830, 1100 cm<sup>-1</sup>; SO<sub>2</sub>: 1362, 1182, 554 cm<sup>-1</sup>; HO-Bande nicht anwesend.

### 2.3.4-D-arabo-Trimethoxy-5-tosyloxy-pentyl-malonsäure-dimethylester (IIb)

Eine auf 0° gekühlte Lösung von 4,85 g 2.3.4-D-arabo-Trimethoxy-5-hydroxy-pentylmalonsäure (Ib) [4] in 50 ml Methanol wurde mit Diazomethan auf übliche Art behandelt, nachher i. V. eingedampft, die auf 0° gekühlte und gerührte Lösung des öligen Rückstandes in 75 ml wasserfreiem Pyridin tropfenweise mit 3,50 g (1,1 mol) Tosylchlorid versetzt und noch 3 Stunden bei Raumtemperatur weiter gerührt. Nachdem das überschüssige Tosylchlorid durch Zusatz von 1 ml Wasser zersetzt worden ist, wurde das Gemisch i. V. eingedampft, der rückständige Sirup durch Schütteln in einem Gemisch von 50 ml Äther und 10 ml Wasser aufgelöst, die wäßrige Phase abgesondert und die Äther-Lösung der Reihe nach mit n-Salzsäure, Wasser, 10% iger Kaliumhydrocarbonat-Lösung und mit Wasser gewaschen, getrocknet (MgSO<sub>4</sub>) und i. V. eingedampft, wobei das Tosylat IIb als bräunlicher Sirup (7,05 g; 88% d. Th.) zurückblieb, der weder kristallisiert, noch in Hochvakuum destilliert werden konnte. Die Substanz ist jedoch zur weiteren Verarbeitung genügend rein.

C20H30O10S (462,48). Ber. S 6,93. Gef. S 6,7%.

#### (3R:4S:5R)-1-Cyan-3.4.5-trimethoxy-cyclohexancarbonsäure-methylester (IIIa)

Eine Lösung von 2.0 g 2.3.4-D-arabo-Trimethoxy-5-tosyloxy-pentyl-cyanessigsäuremethylester (IIa) in 250 ml wasserfreiem Methanol wurde nach Zusatz von 10 mg Natriumjodid und 10 ml 0,48 n methanolischer Natriummethylat-Lösung 24 Stunden bei Raumtemperatur gerührt, dann 16 Stunden unter Rückfluß gekocht und schließlich i. V. eingedampft. Es blieb ein mit Kristallen durchsetztes Öl zurück, das viermal mit je 20 ml Äther ausgezogen wurde. Man wusch die erhaltene Lösung mit Wasser und dampfte sie nach dem Trocknen  $(MgSO_4)$  ein. Der ölige Rückstand lieferte bei der Hochvakuumdestillation (Sdp. 100-110°/ 5×10<sup>-5</sup> mm) 0,75 g (62,5% d. Th.) eines analysenreinen Produktes, das als farbloses Öl anfiel.  $n_D^{2D} = 1,4653$ .  $[\alpha]_D^{2D} = -35,4^{\circ}$  (c = 5,26; Methanol).  $C_{12}H_{19}O_5N$  (257,23). Ber. C 56,01; H 7,45; O 31,09; N 5,44. Gef. C 56,1; H 7,5; O 30,7;

N 5,6%.

IR-Spektrum: Ester C=O: 1750 cm<sup>-1</sup>; Ester C-O: 1200 cm<sup>-1</sup>; NMR-Spektrum: CH(OCH<sub>3</sub>) und (COO)CH<sub>3</sub> zusammengeflossen:  $\delta = 3,78$  ppm; (O)CH<sub>3</sub>:  $\delta = 3,4-3,6$  ppm; -CH<sub>2</sub>- $\delta = 2,1-2,4$  ppm; Protonen einer terminalen  $H_2C = C < Gruppe$  sind nicht nachweisbar.

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#### (3R:4S:5R)-3.4.5-Trimethoxy-cyclohexan-1.1-dicarbonsäure-dimethylester (IIIb)

Eine bei Raumtemperatur gerührte Lösung von 5,00 g 2.3.4-D-arabo-Trimethoxy-5-tosyloxy-pentyl-malonsäure-dimethylester (IIb) in 500 ml wasserfreiem Methanol wurde nach Zusatz von 0,1 g Natriumjodid mit 8,5 ml einer 1,354n methanolischen Natriummethylat-Lösung tropfenweise versetzt, dann noch 8 Stunden weiter gerührt und schließlich 10 Stunden rückfließend gekocht. Die i. V. eingedampfte Lösung lieferte ein mit Kristallen durchsetztes Öl, das nach Zusatz von 15 ml Wasser zuerst mit 50 ml, danach mit 25 ml Äther extrahiert wurde. Die mit 5 ml Wasser gewaschene und getrocknete (MgSO<sub>4</sub>) Lösung hinterließ beim Eindampfen ein hellgelbes Öl, das in Hochvakuum destilliert in Form eines farblosen Öles Eindampten ein heligeibes OI, das in Hochvakuum destilliert in Form eines farbiosen Oies ein analysenreines Produkt lieferte. Sdp. 110–120°/5  $\cdot 10^{-5}$  mm. Ausbeute 2,01 g (63,7% d. Th.).  $n_D^{sp} = 1,4576; d^{20} = 1,14$  g/ml.  $[\alpha]_D^{sp} = -6,1^{\circ}$  (c = 6,24; Methanol).  $C_{13}H_{22}O_7$  (290,32). Ber. C 53,78; H 7,64; O 38,58; CH<sub>3</sub>O 53,45. Gef. C 53,4; H 7,7; O 38,7; CH<sub>3</sub>O 52,5%. Mgew. 293 (Rast). IR-Spektrum: Ester C=O: 1745 cm<sup>-1</sup>; Ester C-O: 1200 cm<sup>-1</sup>; CH<sub>3</sub>O: 2825, 1100 cm<sup>-1</sup>;

?:  $1640 \text{ cm}^{-1}$ .

NMR-Spektrum: CH(OCH<sub>3</sub>) und (COO)CH<sub>3</sub> zusammengeflossen:  $\delta = 3,88$  ppm; (0)CH<sub>3</sub>:  $\delta = 3,35-3,55$  ppm; -CH<sub>2</sub>-:  $\delta = 2,10-2,40$  ppm; Protonen einer terminalen H<sub>2</sub>C = C < Gruppe sind nicht nachweisbar.

### (3R:4S:5R)-1-Cyan-3.4.5-trimethoxy-cyclohexan-carbonsäure (IIId)

Eine Lösung von 1,28 g des Methylesters IIIa in 20 ml Methanol wurde nach Zusatz von 8,0 ml n-Natronlauge 5 Stunden rückfließend gekocht, hierauf i. V. eingeengt, dann mit n-Salzsäure angesäuert und schließlich mit Chloroform ausgezogen. Der nach dem Vertreiben des Chloroforms zurückgebliebene Rückstand wurde mit Äther zu einem Kristallgut zerrieben, das aus Essigester zu einem analysenreinen Produkt kristallisiert werden konnte. Ausbeute 0,82 g (67% d. Th.). Schmp. 164-166°.

C<sub>11</sub>H<sub>17</sub>O<sub>5</sub>N (243,27). Ber. C 54,31; H 7,04; N 5,75; O 32,89; CH<sub>3</sub>O 38,30. Gef. C 54,4; H 7,2; N 6,0; O 32,8; CH<sub>3</sub>O 38,0%. Äquivalentzahl: 244. 2R-Spektrum: Dimere Carbonsäure HO: 3400-2700 cm<sup>-1</sup>; C=O: 1763 cm<sup>-1</sup>; CH<sub>3</sub>O:

I855, 1110 cm<sup>-1</sup>; CN: 2245 cm<sup>-1</sup>.

#### (3R:4S:5R)-3.4.5-Trimethoxy-cyclohexan-1.1-dicarbonsäure (IIIc)

a) Aus dem Dimethylester IIIb. Eine Lösung von 12,60 g des Dimethylesters IIIb in 60 ml Methanol wurde nach Zusatz von 20 ml 50% iger Kalilauge 6 Stunden rückfließend gekocht, die eingeengte Lösung mit 150 ml Wasser verdünnt, mit 50 ml Äther ausgeschüttelt, der wäßrige Anteil nach dem Ansäuern i. V. eingedampft, der feste Rückstand über Phosphorpentoxyd getrocknet und mit heißem, wasserfreiem Alkohol ausgezogen. Nach dem Vertreiben des Lösungsmittels blieb ein Sirup zurück, der mit wasserfreiem Äther zu Kristallen verrieben werden konnte. Ausbeute 8,40 g (73% d. Th.). Zur Analyse wurde eine kleine Probe aus Eisessig umkristallisiert. Schmp. 180–181°.  $[\alpha]_D^{20} = +4^\circ$  (c = 2,00; Alkohol).

C11H17O7 (262,65). Ber. C 50,38; H 6,92; CH3O 35,55. Gef. C 50,3; H 6,9; CH O 35,0%. Äquivalentzahl: Ber. 131,32. Gef. 135.

b) Aus dem Methylester IIIa. Eine Lösung von 25,5 g des Methylesters IIIa in 150 ml Methanol wurde nach Zusatz von 50 ml 50% iger Kalilauge bis zum Aufhören der Ammoniak-Entwicklung (rund 48 Stunden) rückfließend gekocht, dann die alkalische Lösung so verarbeitet wie unter a) angegeben. Ausbeute 14,85 g (68% d. Th.). Schmp. und Mischschmp. mit der nach a) gewonnenen Verbindung 181-182°.

### (3R:4S:5R)-3.4.5-Trimethoxy-cyclohexan-carbonsäure. Gemisch des Trimethyläthers der Dihydroshikimisäure und der Epidihydroshikimisäure (IVa + Va)

In einem kleinen, zur Kurzweg-Vakuumdestillation dienenden Kolben [vgl. 2] wurden 2,35 g der kristallinen 1.1-Dicarbonsäure IIIe mit Hilfe eines Ölbades 30 Minuten auf 200  $^\circ$ erhitzt. Nach dem Abflauen der Gasentwicklung wurde der zurückgebliebene Sirup im selben Kolben bei einer Badtemperatur von 130-140° der Kurzweg-Vakuumdestillation bei 0,05 Torr unterworfen. Ausbeute 1,68 g (85,8% d. Th.) des analysenreinen Mischproduktes.  $n_{22}^{22}$ 1.4693.

 $C_{10}H_8O_5$  (218,25). Ber. C 55,03; H 8,31; CH<sub>3</sub>O 42,66. Gef. C 55,1; H 8,4; CH<sub>3</sub>O 41,8%. Äquivalentzahl: 216.

#### Trennung des 3.4.5-Tri-O-methyl-dihydroshikimisäure-methylesters (IVb) und des 3.4.5-Tri-O-methyl-epidihydroshikimisäure-methylesters (Vb)

Die methanolische Lösung des Gemisches der diastereomeren Carbonsäuren IVa und Va wurde auf übliche Art mit einer Äther-Lösung von Diazomethan behandelt und das nach dem Eindampfen erhaltene Gemisch der diastereomeren Methylester IVb und Vb in 0,30 g Anteilen der chromatographischen Trennung unterworfen. Es wurde eine  $12 imes300~\mathrm{mm}$  Säule aus Kieselgel 0.05-0.2 mm (Merck) angewandt, die mit  $4\frac{9}{0}$  Wasser angefeuchtet worden ist; Eluierung mit wasserfreiem Äther, Fraktionen von je 2 ml. Es enthielten die Fraktionen: 1-4 keine Substanz, 5-10 als Reinsubstanz Vb, 11-13 ein Gemisch von IVb + Vb, 14-30als Reinsubstanz IVb. Auf diese Weise wurden aus 4,72 g des Estergemisches IVb + Vb 2,50 g des 3.4.5-Tri-O-methyl-epidihydroshikimisäure-methylesters (Vb) und 1,90 g des 3.4.5-Tri-O-methyl-dihydroshikimisäure-methylesters (IVb) gewonnen. Durch eine Kurzweg-Vakuumdestillation konnten beide Produkte in analysenreinen Zustand gebracht werden. Sdp. 110-115°/0,05 Torr. Ausbeuten an Reinprodukten: 2,37 g Vb und 1,78 g IVb, d. h. insgesamt 88% auf die Menge (4,72 g) des angesetzten Estergemisches berechnet. Mengenverhältnis der gewonnenen Reinprodukte IVb : Vb = 1 : 1.33.

**IVb**:  $[\alpha]_D^{s_0} = -53^\circ$  (c = 0,500; Cyclohexan)

**Vb**:  $[\alpha]_D^{s_0} = -45^\circ$  (c = 0.511; Cyclohexan)

C<sub>11</sub>H<sub>20</sub>O<sub>5</sub> (233,28). Ber. C 56,86; H 8,68; O 34,45. IVb: Gef. C 56,7; H 8,4; O 35,0. Vb: Gef. C 57,0; H 8,8; O 34,6%.

Gleiches IR-Spektrum von IVb und Vb: Ester C=0: 1740 cm<sup>-1</sup>; Ester C-0: 1200 cm<sup>-1</sup>; CH<sub>2</sub>O: 2825, 1105 cm<sup>-1</sup>.

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# AN IMPROVED METHOD FOR THE SYNTHESIS OF THE THYROTROPIN RELEASING HORMONE (TRH)

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The key compound of the new TRH synthesis, Z-Pyr-His-Pro-NH-Mbh, was prepared by a stepwise route starting from the C-terminal residue. Homogeneous TRH was directly obtained from the crystalline protected tripeptide amide.

The thyrotropin releasing hormone (TRH) has been isolated from porcine [1] and ovine [2] hypothalami and proved to be identical with L-pyroglutamyl-L-histidyl-L-proline amide [3—8]. Synthetic routes for TRH by either conventional methods, *i.e.* by fragment coupling in solution, or by solid-phase techniques have been discussed in several papers [e.g. 6—13].

Apart from the biological significance of TRH, the comparatively large number of publications indicates that the synthesis of this tripeptide amide is not as simple as it seems at first sight. The pure end-product could only be obtained by chromatography (or by countercurrent distribution in the earlier methods) if carefully purified intermediates were used in the coupling steps. At the same time, the isolation and working-up of the intermediate products were rather difficult.

For a comparison of the different synthetic procedures leading to TRH, the "efficiency"  $(E_f)$  of the syntheses was calculated according to the equation [14]:

$$E_f = rac{n \cdot m_{pp} \cdot 100}{m_{Ad}}$$

where *n* is the number of amino acid residues in the peptide chain,  $m_{pp}$  is the number of moles of pure product obtained, and  $m_{Ad}$  is the total number of moles of amino acid derivatives used in the synthesis. This expression of efficiency is based on the utilization of amino acid derivatives (instead of amino acids, as proposed originally by RYDON [14]).

Calculations based on the published data show that the conventional syntheses (in solution) are more efficient in general than those performed on a solid support, as in the latter case the acylating components have to be used in large excess. The most efficient procedure of the solid-phase synthesis of TRH reported by BEYERMAN [13] has an  $E_f$  value of 22%, while the efficiency

of the best accomplished conventional synthesis published by FLOURET [9] is 52% (it should be noted that 3.25% was calculated for FLOURET's solidphase synthesis). The low efficiency of the solid-phase synthesis was to be expected, nevertheless this technique seemed to be promising for the preparation of TRH, because the problematic isolation of intermediates was eliminated. Of course, the purification of the end-product could not be omitted.

The present synthesis of TRH uses a stepwise method in solution, starting with the C-terminal of the tripeptide. Carbobenzoxylation was used for the protection of the  $\alpha$ -amino groups and the imidazole-nitrogen in histidine, and the *p*,*p*'-dimethoxybenzhydryl group [15] for permanent blocking of the C-terminal amide bond. Substitution of the amide by a highly hydrophobic group led to a radical change in the hydrophilic character of intermediates. (The significance of using substituted amide group in the synthesis of highly hydrophilic peptide amides will be discussed and demonstrated in a separate paper [16].) Owing to this fact, purifications by chromatography could be omitted, in contrast with all TRH syntheses published so far. The procedure is outlined in Fig. 1.\*



Fig. 1. Scheme of the TRH synthesis

Proline-p,p'-dimethoxybenzhydryl amide (I) obtained from the corresponding carbobenzoxy derivative was allowed to react with 2,4,5-trichlorophenyl dicarbobenzoxyhistidinate (II) to yield the protected dipeptide amide (III), which was converted into the crystalline oxalic acid salt of IV. The latter gave with 2,4,5-trichlorophenyl carbobenzoxypyroglutamate the crystalline protected tripeptide amide V. Compound V was treated with hot trifluoroacetic acid, and the resulting trifluoroacetate salt was converted into acetate

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<sup>\*</sup> The symbols follow the Tentative Rules of the IUPAC-IUB Commissions on Biochemical Nomenclature (J. Biol. Chem. 241 (1966) and 242, 555 (1967). The following additional abbreviations have been used: OTCP=2,4,5-trichlorophenyloxy, Mbh=p,p'-dimethoxybenzhydryl.

by an anion exchange resin (acetate form). The TRH, obtained as a white microcrystalline powder, was homogeneous on TLC and electrophoresis. The efficiency of this synthesis was 52%.

### Experimental

All melting points are uncorrected. TLC was performed on Silicagel G using the following solvent systems: 1: chloroform/n-hexane/acetic acid (8:1:1); 2: ethyl acetate/pyridine/ acetic acid/water (60:20:6:11); 3: n-butanol/ethyl acetate/acetic acid/water (1:1:1:1). Electrophoresis was referred to the migration of His in pyridine acetate at pH 6.5 ( $E_{6.5}^{His}$ ).

### Carbobenzoxy-L-proline-p,p'-dimethoxybenzhydrylamide

Carbobenzoxyproline amide [17] (31.6 g; 127 mmoles) and p,p'-dimethoxybenzhydrol (34.2 g; 140 mmoles) were dissolved in glacial acetic acid (320 ml) and after adding 0.7 ml of conc. sulfuric acid, the solution was kept at room temperature for three days. The reaction mixture was poured into water (5000 ml); the resulting emulsion was extracted with ethyl acetate. The organic layer was washed with sodium bicarbonate and water, then dried and evaporated in vacuum. The residue crystallized on trituration with diisopropyl ether to yield 49.6 g (82.5%) of the product, m.p. 119–121 °C;  $[\alpha]_{22}^{22}$  13.2° (c = 2, dimethylformamide); Rf 0.7-0.8.

 $C_{28}H_{30}O_5N_2$  (474.54). Calcd. C 70.86; H 6.37; O 16.85; N 5.90. Found C 70.3; H 6.3; O 16.9; N 6.0%.

#### L-Proline-p,p'-dimethoxybenzhydrylamide oxalate (I)

Protected proline amide (34.18 g; 72 mmoles) was suspended in methanol (350 ml) and hydrogenated over palladized charcoal. The catalyst was removed by filtration, and after adding anhydrous oxalic acid (6.5 g; 72 mmoles), the solution was evaporated to dryness. The residue was crystallized from ether to obtain 29.3 g (91.5%) of I<sub>2</sub> m.p. 201-202 °C;  $\begin{array}{c} R_{f}^{2} \ 0.4 - 0.5; \ [\alpha]_{D}^{22} - 24.2^{\circ} \ (c = 1, \ 95\% \ \text{acetic acid}). \\ C_{22}H_{26}O_{7}N_{2} \ (430.44). \ \text{Calcd. C 61.38; H 6.09; O 26.01; N 6.50. Found C 61.38; H 6.25; } \end{array}$ 

O 26.04; N 6.73%.

#### 2,4,5-Trichlorophenyl dicarbobenzoxy-L-histidinate (II)

A solution of dicarbobenzoxyhistidine methanolate [18] (92.0 g; 200 mmoles) in chloroform was evaporated in vacuum. The residue was then redissolved in chloroform (200 ml) and treated with 2,4,5-trichlorophenol (43.5 g; 220 mmoles) and dicyclohexylcarbodiimide (41.2 g; 200 mmoles) at 0 °C. The mixture was kept at room temperature overnight, filtered and the filtrate evaporated in vacuum. The residue was triturated with ether, filtered, washed with ether and dried. The crude product was crystallized from a mixture of ethyl acetate and petroleum ether to yield 79 g (65.5%) of II; m.p. 109–112 °C;  $R_{f}^{i}$  0.75–0.85;  $[\alpha]_{20}^{20}$  –6.46° (c = 1, chloroform).

C28H22O6N3Cl3 (602.85). Caled. C 55.78; H 3.67; O 15.92; N 6.80; Cl 17.64. Found C 55.68; H 3.79; O 16.04; N 6.95; Cl 17.54%.

#### L-Histidyl-L-proline-p,p'-dimethoxybenzhydrylamide dioxalate (IV)

To a stirred suspension of I (43.0 g; 100 mmoles) in dimethylformamide (100 ml) an equivalent of triethylamine (24.0 ml; 200 mmoles) and 2,4,5-trichlorophenyl dicarbobenzoxy-L-histidinate (60.3 g; 100 mmoles) were added. The reaction mixture was allowed to stand overnight and concentrated in vacuum. The residue was dissolved in ethyl acetate and water, the organic layer was washed with water and dried. The solution was evaporated in vacuum and the residue triturated with ether, filtered off, and washed with ether and n-hexane to yield 63.0 (84.5%) of the protected dipeptide amide III,  $R_f^2 0.40 - 0.45$ . The product thus obtained was dissolved in methanol (500 ml) and hydrogenated over palladized charcoal. The catalyst was filtered off, and after adding anhydrous oxalic acid (15.2 g; 169 mmoles) to the filtrate, it was evaporated. The residue was crystallized from ether to obtain 54.45 g (98%) of IV, m.p. 122–124 °C;  $R_f^* 0.25-0.35$ ;  $[\alpha]_D^{z_0} - 8.5^\circ$  (c = 1, methanol).

 $C_{30}H_{35}O_{12}N_5$  (657.62). Calcd. C 54.79; H 5.36; O 29.34; N 10.64. Found C 54.64; H 5.46; O 29.10; N 10.76%.

### Carbobenzoxy-L-pyroglutamyl-L-histidyl-L-proline-p,p'-dimethoxybenzhydrylamide (V)

To a solution of IV (50.0 g; 76 mmoles) in dimethylformamide (150 ml) containing equivalent triethylamine (42.7 ml; 305 mmoles) 2,4,5-trichlorophenyl carbobenzoxy-L-pyroglutamate [19] (33.7 g; 76 mmoles) was added, and the reaction mixture was kept at room temperature overnight. The solution was evaporated in vacuum and the residue triturated with ether, filtered off and washed with ether. The crude product was crystallized from hot methanol and water to yield 38.5 g (70%) of V<sub>2</sub>; m.p. 127-128 °C; R<sup>2</sup><sub>1</sub>0.60-0.65; [a]<sup>2</sup><sub>10</sub>-34.6° (c = 1, dimethylformamide).

C38H42O9N6 (722.77). Calcd. C 64.81; H 5.85; O 17.70; N 11.62. Found C 64.60; H 5.95; O 17.65; N 11.77%.

#### L-pyroglutamyl-L-histidyl-L-proline amide acetate (TRH)

The protected tripeptide amide V (36.2 g; 50 mmoles) was dissolved in trifluoroacetic acid (100 ml) and after adding anisole (10 ml), the solution was boiled for 1 hr. The solution was cooled to room temperature and diluted with ether. The precipitate which formed was filtered off and washed with ether, dried, then redissolved in methanol (200 ml). The solution was stirred with Amberlite IR 4B resin (acetate cycle) for 2 hrs. The resin was removed by filtration an washed with 0.06 N acetic acid. The filtrate and washing were combined and evaporated in vacuum to dryness. The residue was triturated with ether, filtered off, washed with ether and dried to give 18.92 g (86%) of TRH;  $R_t^s$  0.25—0.30;  $E_{6.5}^{His}$  0.8;  $[\alpha]_D^{ss}$  -40.3° (c = 1, 95% acetic acid), -60.5° (c = 1, water).

C16H22O4N6 · CH3COOH (422.44). Calcd. C 51.18; H 6.20; O 22.72; N 19.84. Found C 51.11; H 6.33; O 22.67; N 19.89%

Amino acid analysis: Glu 1.04 (1); His 1.09 (1), Pro 1.00 (1).

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# THE ALKALOIDS OF AMSONIA ANGUSTIFOLIA, I (PRELIMINARY COMMUNICATION)

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Received October 10, 1972

In 1964 (—)-tabersonine and  $\beta$ -yohimbine were isolated by TOMCZYK [1] from the seeds and roots, respectively, of Amsonia angustifolia belonging to the Apocynaceae family. In this paper we report the isolation and structure identification of some alkaloids found by us in the stem and leaves of the plant, namely (+)-vincadifformine (1) [2], [3], (—)-lochnericine (2) [4] and (—) tabersonine (3) [4].



The aqueous solution of the extract obtained by means of metanolic percolation from the stem and leaves of the plant was extracted with *n*-hexane at pH 3.5. The *n*-hexane extract was evaporated to dryness, the residue was dissolved in chloroform, then extracted with 0.5 N sulfuric acid.

The solution obtained was made slightly alkaline (pH 9), then it was extracted with CHCl<sub>3</sub> to obtain a crude alkaloid mixture.

Amorphous (+)-vincadifformine was isolated from the mixture on preparative Kieselgel (MeOH: ethyl acetat : benzene 1:5:30) then on aluminium oxide (ether : benzene : cyclohexane 1 : 2 : 2).  $[\alpha]_{\rm D} + 605^{\circ} (c = 0.21\%, \text{ EtOH}), \lambda_{\rm max}^{\rm EtOH} 230 \text{ nm}$ (lg  $\varepsilon 4.00$ ), 304 nm (lg  $\varepsilon 4.02$ ), 330 nm (lg  $\varepsilon 4.20$ ).

IR (KBr): 3470, 1685, 1620 and 745 cm<sup>-1</sup>.

The 70 eV mass spectrum of the substance was in agreement with the mass spectrum data reported for vincadifformine [4]; only two intense peaks appear in the spectrum: m/e 338 (M, 16%), m/e 124 (100%); the formula of the molecular ion is  $C_{21}H_{26}N_2O_2$ . (M m/e measured: 338, 1992).

(—)-Lochnericine was isolated according to the above procedure from the chloroform fraction containing the weak bases.  $[\alpha]_D$ —473 (c = 0.37, EtOH). M.p. 188—191° (EtOH).  $\lambda_{\max}^{EtOH}$  230 nm (lg  $\varepsilon$  4.04), 303 nm (lg  $\varepsilon$  4.12, 332 nm (lg  $\varepsilon$  4.30). The infrared spectrum was identical with that given for lochnericine in the spectrum catalogue of HOLUBEK *et al.* [6]. The high-resolution mass spectrometric investigations are in agreement with the structures suggested for lochnericine [7].\*

The 70 eV mass spectrum was the following:

m/e	I, %	Formula
352	45	$\mathrm{C}_{21}\mathrm{H}_{24}\mathrm{N}_{2}\mathrm{O}_{3}$
323	7.8	 $\mathbf{C_{19}H_{19}N_2O_3}$
322	11	$\mathbf{C}_{22}\mathbf{H}_{22}\mathbf{N}_{2}\mathbf{O}_{2}$
293	5.0	
214	37	
138	100	$C_8H_{12}NO$
108	83	$C_7H_{10}N$

Two of the three oxygen atoms of the molecule are in a methoxycarbonyl group (see the ion peak of mass number 293 (M - 49)); the third oxygen can be attached to the C<sub>6</sub>-C<sub>7</sub>-C<sub>8</sub> atoms on the basis of the appearance of the ions of mass number 138 and its complementary of mass number 214 produced on splitting of the C<sub>4</sub>-C<sub>5</sub> and C<sub>10</sub>-C<sub>11</sub> bonds, and also considering the appearance of ion  $M - C_2H_5$  (m/e 323). The readily occurring loss of formaldehyde from the molecular ion and from the ion species of mass number 138 can be explained with the presence of an epoxy group very prone to rearrangement.

Amorphous (-)-tabersonine was also isolated from the weak base (chloroform) fraction according to the procedure described for (+)-vincadifformine.

\* Of the mass spectrum of lochnericine only the mass number of the base peak  $(m/e \ 138)$  has been reported [6].

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 $[\alpha]_{\rm D}$  –260° (c = 0.66%, EtOH),  $\lambda_{\rm max}^{\rm EtOH}$  226 nm (lg  $\varepsilon$  4.00), 300 nm (lg  $\varepsilon$  3.98), 332 nm (lg  $\varepsilon$  4.15). IR (KBr): 3470, 1680, 1615, 747 cm<sup>-1</sup>.

The 70 eV mass spectrum was the following: m/e 336 (M, 48%), 305 (5%), 229 (32%), 135 (100%), 122 (36%), 121 (31%), 108 (27%), 107 (49%). The formula of the molecular ion is  $C_{21}H_{29}N_2O_2$  (m/e measured = 336.1836).

The mass spectrum is very similar to that of 2,3-dihydrotabersonine [7]. A striking difference is the absence of the following ions: M-86, *i.e.* the ion peak, corresponding to the elimination of methyl acrylate from the molecular ion, and the ion peaks m/e 130 and 144. This can be explained by the presence of a C<sub>2</sub>-C<sub>3</sub> double bond.

The plants were supported by the Botanical Research Institute of the Hungarian Academy of Sciences, Vácrátót.

The mass spectra were recorded by an MS-902 (AEI) mass spectrometer; the accuracy of the high-resolution mass measurements is 2-3 ppm.

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#### РЕЗЮМЕ

# Измерение небольших поверхностей адсорбционным методом с газом-носителем

К. ОЛА, ДЬ. ГАШПАР и С. БЁРЁЦ

Описывается установка для измерения адсорбции с газом-носителем, которая имеет различные преимущества перед ранее описанной. Система потока газа была модифицирована так, что состав смеси газов, проходящих через детектор, остается неизменным и в случае различных составов газовой смеси, прошедшей через адсобционный сосуд. Была установлена погрешность, возникающая за счет нелинейности детектора. Изучая зависимость между скоростями сорбции или десорбции и сигналом детектора, было установлено, что зависимость между площадью регистрируемой полосы и количеством десорбированного азота является неоднозначной, и зависит от формы концентрационной волны во времени. Была рассчитана максимальная относительная погрешность в зависимости от навески.

# Влияние сопротивления раствора в полярографии переменного тока для случая электродного процесса, контролируемого диффузией

Й. ДЕВАИ, Т. ГАРАИ, Л. МЕСАРОШ и Б. ПАЛАДИ-ФЕНЕШ

Экспериментально были проверены ранее выведенные зависимости первого, второго и третьего компонентов переменного тока, возникающего на электроде поляризованном напряжением переменного тока, суперпонируемом на напряжение постоянного тока. Данные зависимости принимают в учет влияние напряжения, установливающегося на сопротивлении раствора в случае электродных процессов, контролируемых диффузией. Результаты измерений, относящиеся к системам Fe(III)/Fe(II) и Pb(II)/Pb(Hg), в пределах ошибки измерений согласуются с расчетными данными. Отклонения, превышающие погрешность измерений, наблюдались для систем Tl(I)/Tl(Hg) и Cd(II)/Cd(Hg). Расхождения между рассчитанными и измеренными величинами основного, а также второго гармонического компонентов в области более отрицательных потенциалов полуволны для систем Tl(I)/Cd(Hg) — изменением велиситем согов.

# Исследование некоторых структурных особенностей гидратов паравольфрамата с помощью ИК спектрофотометрии

#### Б. А. КИШШ

В области 400—4000 см<sup>-1</sup> были сняты и рассмотрены ИК спектры гидратов паравольфрамата, а также дейтерированного аммонийпаравольфрамат-5-гидрат. Было найдено, что в области частот W—O колебаний, наблюдаемые полосы обладают почти одинаковыми частотами, контурами и отношениями интенсивностей. Спектр микрокристаллических солей, с очень хорошим приближением, не зависит от симметрии групп в углах кристаллической решетки. В области валентных колебаний конечных W—O групп были найдены лишь следующие отклонения: полоса 28- и 11-гидратов в области 940 см<sup>-1</sup> в случае 7-гидрата расщепляется на две, а в случае 5-гидрата на три полосы. Это расщепление объяснялось дифференциированием различных W—O (1) типов связей с уменьшением содержания гидрата. Было установлено, что паравольфраматы содержат также структур- ные OH-группы в малых количествах.

Термоконденсационные и спектроскопические исследования однозначно указывают на то, что среди основных структур Линдквиста  $[W_{12}O_{46}]^{-20}$  и Липскомба  $[W_{12}O_{42}]^{-12}$ , последняя находится в согласии с экспериментальными данными. Таким образом, структура паравольфрамат-аниона может быть описана общей формулой  $[W_{19}O_{40}(OH)_9]^{-10}$ .

# Исследование восстановления и окисления ацетальдегида и пропиональдегида на платинированном платиновом электроде

#### дь. хорани и М. новак

Электровосстановление и электроокисление ацетальдегида и пропиональдегида изучалось в кислом — 1N  $HClO_4$  — растворе на платинированном платиновом электроде. Было установлено, что в процессе электрогидрирования в значительных количествах образуются этан и пропан, соответственно. Результатом процесса окисления являются соответствующие карбоновые кислоты. Указываются трудности, связанные с определением стационарных поляризационных кривых.

#### Термодинамические зависимости изотопных молекул диборана

### Б. ВИЗИ и С. Й. СИВИН

На основе спектроскопических данных были рассчитаны термодинамические зависимости изотопных молекул диборана с помощью модели гармонического осциллятора с жестким ротатором. Приводятся зависимости С<sup>\*</sup><sub>mp</sub>, S<sup>\*</sup><sub>m</sub>, (H<sup>\*</sup><sub>m</sub>-E<sub>m</sub>)/Т и – (G<sub>m</sub>-E<sup>\*</sup><sub>m</sub>)/Т в интервале температур от 100 до 1000°К через каждые 100°.

# Электронографическое исследование строения молекулы этан-1,2-дитиола

#### дь. ШУЛЬЦ и И. ХАРГИТТАИ

Геометрия и поворотная изомерия молекулы этан-1,2-дитиола были изучены в газовой фазе с помощью электронной диффракции. Анти и гош конформеры вокруг связи С—С находятся с относительным содержанием 62 и 38%-ов, соответственно. Форма гош может быть получена из формы анти поворотом одной из групп SH вокруг связи С—С на 106°.

# Простой метод определения скорости коррозии

Й. ДЕВАИ, Л. МЕСАРОШ, Ф. ЯНАСИК и САЕД САБЕТ АБД ЭЛЬ РЕХИМ

Был модифицирован метод измерения скорости электрохимической коррозии металлов, основанный на определении поляризационного сопротивления. Было измерено сопротивление ячейки, содержащей два одинаковых электрода, откуда, зная сопротивление электролита, может быть определено поляризационное сопротивление. Преимущество данного метода по сравнению с методом, основанном на измерении поляризационных кривых, заключается в том, что нет необходимости в использовании электрода сравнения. Таким образом, данный метод может быть широко использован для измерения коррозии, протекающей в органических растворителях, лаках, красках и сплавах.

### ИК спектроскопические исследования морфина, І

3. ДЫНЯ, Ш. МАКЛЕЙТ, Ш. САБО, Т. МИЛЕ и Р. БОГНАР

Были сняты ИК спектры кодеина(IA) и дигидрокодеина(IIA), а также их производных. Рассматривается возможность использования данного метода для определения структуры С-кольца, а также разрешения вопросов пространственного строения.

Было установлено, что

 Насыщенный или ненасыщенный характер С-кольца может быть установлен из ИК спектров совершенно однозначно.

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— Для ненасыщенных соединений, замещенных в позициях С<sub>6</sub>—X и С<sub>8</sub>—X, характерные изменения были найдены в области 800—1000 см<sup>-1</sup>. В этой области, в случае закрытого Е-кольца, наблюдаются полосы высокой интенсивности, обозначенные через «Е-полосы»: для С<sub>6</sub>—X заместителей при частотах 940 ± 10см<sup>-1</sup>, а для С<sub>8</sub>—X заместителей при частотах 900 ± 13 см<sup>-1</sup>.

— Полосы, характеризующие C<sub>6</sub>—Х заместители в изученных соединениях, соответственно их предполагаемой структуре пространстенной, появляются в области, согласующейся с литературными данными.

— На основе полученных данных, в случае соединений, содержащих С-кольцо в насыщенной форме и заместители С<sub>6</sub>—Х в аксиальном положении, полагалось гипотетическое конформационное равновесие, которое представляет собой равновесие между молекулами, содержащими С-кольцо в форме стула и «гибкой ванны».

#### Реакции соединений осмия с аминокислотами

#### я. нилаши и п. оршош

Было исследовано окисляющее действие  $OSO_4$  и  $K_2OSO_4$  на аминокислоты в среде 0,5 NaOH при 100°C. Было установлено, что при реакции тетраокиси осмия с аминокислотами — за исключением пролина, оксипролина,  $\beta$ -аланина и  $\gamma$ -аминомасляной кислоты — выделяется в два раза больше аммиака, чем под действием осмата калия. Оба соединения осмия при этом восстанавливаются до диокиси осмия.

Подробно изучая реакцию деаминирования гликоколя и  $\alpha$ -аланина, было установлено, что в первом случае помимо аммиака выделяется также глиоксильная кислота, которая сразу окисляется до щавелевой кислоты. Продуктом окисления  $\alpha$ -аланина является, помимо аммиака, пировиноградная кислота, окисление которой до двуокиси углерода и уксусной кислоты является медленным процессом.

На основе до сих пор полученных результатов полагалось, что под влиянием  $OSO_4$ и  $K_2OSO_4$  на аминокислоты образуются аммиак и соответствующие кетокислоты. Степень выделения аммиака определяется отношением скоростей образования аммиака и кетокислоты, а также скоростью дальнейшего окисления кетокислоты.

### Синтез дигидросикимикислота- и эпидигидросикимикислотатриметилэфиров из 0-арабинозы, V

#### Новые производные О-арабинозы

я. ЧАСАР и ДЬ. БРУКНЕР

Приводятся синтезы дигидросикимикислота-триметилэфира (IVa) и эпидигидросикимикислота-триметилэфира (Va), а также их метиловых эфиров (IVb и Vb, соответственно). Исходным соединением синтеза был метиловый эфир 2,3,4-0-арабо-триметокси-5-тозилоксипентилциануксусной кислоты (IIa), а также аналогичный малоновый эфир (IIb), полученные из 0-арабинозы. Оба соединения с помощью циклизации за счет этилата натрия могут быть превращены в циклогексановые производные III а и IIIb, соответственно, щелочной гидролиз которых приводит к одному и тому же продукту, а именно к (3R : 4S : 5R)-3,4,5-триметоксициклогексан-1,1-дикарбоновой кислоте (IIIc). Термическое декарбоксилирование дикарбоновой кислоты дает смесь дигидросикимикислога-триметилэфира (IVa) и эпидигидросикимикислота-триметилэфира (Va). Разделение хроматографией на колонке двух метиловых эфиров карбоновых кислот дает два диастереомера в чистом состоянии.

# Усовершенствованный метод синтеза гормона (TRH) выделяющего тиротропин

#### Ш. БАЮС и И ФАУСТ

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