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РЕЗЮМЕ

Полярографическое определение ионов редкоземельных металлов в растворах, содержащих лактат аммония

Й. ИНЦЕДИ и Л. ЭРДЕИ

Исследовалось полярографическое определение ионов редкоземельных металлов с помощью реакции вытеснения из комплексов. Было установлено, что ионы редкоземельных металлов в растворах с pH = 9, содержащих лактат аммония вытесняют металлические ионы почти в стехиометрическом количестве из комплексов Cu(II)ЭДТУ и Zn(II)-ЭДТУ. Полярографическим определением выделяющихся медных и цинковых ионов осуществляется косвенное определение редкоземельных металлов.

Определение индекса удерживания различных металлоорганических соединений в газовой хроматографии

Г. ГАРЗО, Ю. ФЕКЕТЕ и М. БЛАЖО

Определялись индексы удерживания 68 кремнийорганических и ряда германий и оловоорганических соединений на колонках, в качестве стационарной фазы в которых использовался Апьезон L, силиконовый эластомер марки SE—30, фтористый силикон марки QF—1, жидкий нитрил-силикон марки XF—1112 и о-нитротолуол. Все измерения проводились в соответствии с указаниями „Gas Chromatography Discussion Group Data Sub-committee”.

На основе (а) величин ΔJ, рассчитанных из индексов удерживания для одного-вещества, определенных на различных колонках, и (б) инкриментов (∂J) индекса удерживания, в случае последовательных членов гомологического ряда, для тех же колонок были установлены некоторые правила и взаимоотношения между структурой исследуемых веществ и их газо-хроматографическими характеристиками. Это дает возможности для наиболее подходящего выбора колонок для образцов известного состава или для идентификации пиков в случае образцов неизвестного состава.

Определение оптимального графика и чувствительности активационного анализа без разложения

П. КВИТНЕР и А. МОНТВАИ

Приводится математический метод определения оптимального программирования во времени активации, охлаждения и измерения с целью получения максимально возможной точности на измерение активационного анализа при использовании различных сцинтилляционных детекторов и при наличии заданных интерферирующих и фоновых активностей. Согласно результатам расчетов, определяется максимально возможная чувствительность без химического разделения, лимитируемая статистической девиацией.

Новый метод расчета констант стабильности

Д. ГЕРГЕЙ, Й. НАДЬПАЛ и Й. МОЙЗЕШ

Разрабатывался новый метод расчета констант стабильности. Метод исходит из предположения, что величина площади, получаемая при интегрировании кривой образования между заданными двумя точками — не считая $\bar{n}$ — зависит только от соотношения констант стабильности. Таким образом, величина $\log K_1/K_2$ вычисляется на основе площади, определенной путем графического интегрирования. Из данных по $\log K_1/K_2$, поправка (y), необходимая для расчета констант стабильности, определяется либо расчетом, либо графическим путем.

В таблице приведены величины площадей, соответствующие 19 точкам функции образования в области $\log K_1/K_2 = 0 + 4$ с интервалами значений по 0,2.

Данный метод можно рассматривать по существу как модифицированный метод поправленных термов и может быть использован для расчета $\log K_1/K_2$ и при $N = 2$ и $N = 3$. Возможность применения метода проверялась на расчетах систем Ni(II)-глицин и Cu(II)-глицин. На основе температурной зависимости констант стабильности были рассчитаны соответствующие изменения энтальпии и энтропии для вышеописанных процессов комплексообразования. Эти значения для комплекса Cu(II)-глицин следующие: $\Delta H_1 = -5{,}9$ ккал/моль, $\Delta H_2 = -6{,}5$ ккал/моль, $\Delta S_1 = 18$ е. э., $\Delta S_2 = 11$ е. э., а для Ni(II)-глицин: $\Delta H_1 = -4{,}1$ ккал/моль, $\Delta H_2 = -5{,}3$ ккал/моль, $\Delta S_1 = 13$ е. э., $\Delta S_2 = 4$ е. э. Найденные нами изменения энтальпии хорошо совпадают с литературными данными, определенными калориметрическим путем, в пределах погрешности ± 1 ккал/моль.

Данные по селективности кватернизации соединений со скелетом морфина. Изомеризация четвертичных солей

К. КОЦКА и Г. БЕРНАТ

Изучалась реакция кватернизации морфина (I) с йодистым аллилом, а также N-аллил-нор-морфина (II) с йодистым метилом, используя для оценки препаративный метод и ик-спектроскопию. На основе изоляции четвертичных солей и ик-спектроскопического анализа изолированных фракций и сырых продуктов реакции было установлено, что в обеих реакциях, наряду с образующимися в качестве главных продуктов производными четвертичных солей ((III) и (IV)), образуются также соединения четвертичных солей, стереоизомерные на азоте (IV) и (III), соответственно. При нагревании в хлороформе йодистого морфин-N-аллила (III) и йодистого кодеин-N-бензила (V) происходит частичная изомеризация этих соединений в N-аллил-нор-морфин-метоиодид (IV) и N-бензил-нор-кодеин-метоиодид (VI), соответственно: На основе данных по относительной селективности реакций кватернизации, ик-спектров четвертичной солей и изомеризации следует, что заместитель, вводимый в молекулу четвертичной соли, образующейся в качестве главного продукта при кватернизации, занимает аксиальное положение.

Исследование химических превращений диолов и кольцевых эфиров. XXVII.

Й. САБО, У. КОВАЧ и. М. БАРТОК

При восстановлении, по способу Кижнера-Вольфа, соответствующих гомологов оксэтана и тетрагидрофурана были получены следующие эфиры:

2,2,4,4-тетраметилоксэтан (72%)
2,4 -диметил-2,4-диэтилоксэтан (78%)
2,2,4,4-тетрафенилоксэтан 40%),
2,2,5,5,-тетраметилтетрагидрофуран (66%)
2,5-диметил-2,5-диэтил-тетрагидрофуран (72%)
2,2,5,5,-биспентаметилен-тетрагидрофуран (70%)

Таким образом, разработан новый способ получения трудно доступных α, α′-тетразамещенных эфиров с четырехчленными кольцаму. Наряду с этим расширялась область применения метода Кижнера-Вольфа.

Исследование химических превращений диолов и органических окисей, XIX

М. БАРТОК

Исследовался термический распад 2-моно-замещенных β-окисей, с помощью микрореакторной техники. Скорость термического распада является функцией результирующей индуктивного и сверхсопряженного влияний углеводородных радикалов в α-положении. Образование продуктов пиролиза объясняется как результат двух первичных, а также нескольких вторичных процессов. Главным направлением термического распада (80—90%) является превращение, начинающееся с разрыва связи C—O, находящейся в соседном положении с заместителем, которое приводит к образованию соответствующего алкена-1 и формальдегида. Распад молекулы окиси в две части сопровождается, по всей вероятности, вследствие влияния стенок реактора, изомеризационными процессами, проходящими с образованием соответствующих альдегидов и α, β-ненасыщенных спиртов.

Полимеризация метилметакрилата при высоких степенях превращений, II

Исследование инициирующего влияния перекиси лауроила

И. МОНДВАИ и Й. НАДЬ

Исследовалась блочная полимеризация метилметакрилата при различных температурах в присутствии перекиси лауроила. Определены брутто-константы скорости и энергия активации полимеризации. Установлено, что зависимость предельного превращения от концентрации инициатора и температуры аналогична зависимости, полученной в случае перекиси бензоила, в то время как начало гельэффекта изменяется в значительно меньшей мере с изменением предыдущих параметров. При сравнении двух видов инициатора было установлено, что качество инициатора в значительно большей степени влияет на скорость реакции в начальной стадии полимеризации, нежели при высоких степенях превращений.

Полимеризация метилметакрилата при высоких степенях превращений, III

Исследование замедляющего действия мононитрофенолов

И. МОНДВАИ и Й. ГАЛ

Исследовалась блочная полимеризация метилметакрилата при одинаковых концентрациях инициатора, в присутствии различных количеств замедлителя. Определены параметры замедления, характеризующие исследованные соединения. Установлено, что исследованные соединения в значительно меньшей мере снижают скорость начального участка полимеризации, нежели в области глубокой полимеризации. Наиболее эффективным замедлителем оказался 2-нитрофенол, замедляющее действие которого на один порядок больше, чем двух других исследованных соединений. Эффективности 3-нитрофенола и 4-нитрофенола почти что одинаковы.

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EDITOR'S NOTE

The following papers published in the 50th volume of Acta Chimica have been presented at the "Conference on Application of Physico-Chemical Methods in the Chemical Analysis", Budapest, Hungary, April 20—23, 1966:

BRODA, R. and SCHÖNFELD, T.: Nuclear Methods in Chemical Analysis

DAMS, R. and HOSTE, J.: Determination of Arsenic in Antimony-Iron Matrices by Activation Analysis

KRAFT, G.: The Application of Polarised Electrodes for the End-Point Indication of Titrations

WAINERDI, R. E. and FITE, L. E.: Automatic and Computer-Coupled Nuclear Activation Analysis

The following papers in the same volume have been presented at the "Conference on Some Aspects of Physical Chemistry", Budapest, Hungary, April 25—27, 1966:

BERAK, J. M., GUCZALSKI, R. and WÓJCIK, J.: The Influence of ZnO Promotor on the Activity and Selectivity of the Catalyst in Butadine Synthesis from Ethyl Alcohol

KERTÉSZ, D., KŐRÖSY, F. and SZÉKELY, J.: pH-Dependent Ion-Permselective Membranes

PURNELL, J. H., WASIK, S. P. and JUVET, R. S.: Novel Uses of Gas Liquid Chromatography; the Study of Surface Excess Concentrations and of Complex Formation

RANDIĆ, M., STEFANOVIC D. and KLASINC, L.: Investigation of Hybridization in Methyl Substituted Cyclopropanes by the Method of Maximum Overlap

Acta Chimica Academiae Scientiarum Hungaricae Tomus 51, pp. 1—2 (1967)

ÜBER DEN ALKALIFEHLER DER GLASELEKTRODE

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Eingegangen am 16. März 1966

In ihrer Arbeit: »Über den Alkalifehler der Glaselektrode, III.« [1] haben B. Lengyel und Mitarbeiter zu unseren »Messungen der Aktivitätskoeffizienten der H^+ und Na^+ in der Quellschicht von Glaselektroden« Stellung genommen und, gestützt auf eigene Messungen, die Annahme von Nikolskij u. a., daß der Aktivitätskoeffizient der H^+ konzentrationsunabhängig gleich 1 sei, aufrechterhalten, indem sie für unsere Meßergebnisse bezüglich der Aktivität der H^+ Meßfehler verantwortlich machen. Dazu ist folgendes festzustellen:

Es kann bestätigt werden, daß der relative Fehler der Bestimmung von f'_{H^+} — vor allem für kleine Werte von X_{H^+} — nach unserer Methode groß ist. Eine Fehlerabschätzung unserer Meßwerte zeigt jedoch, daß z. B. für $X_{H^+} = 0{,}16$ der Aktivitätskoeffizient der H^+ in der Quellschicht mit Sicherheit noch unter 0,5 liegt und somit eine starke Abweichung von dem für die reine H-Funktion festgelegten Wert $f'_{H^+} = 1$ zeigt. Unsere experimentellen Ergebnisse sprechen daher *für* eine Abhängigkeit des f'_{H^+} von der Zusammensetzung der Quellschicht.

Wenn auch mit kleineren Werten von X_{H^+} der Fehler von f'_{H^+} größer wird, so ist doch die Annahme, daß für $X_{H^+} = 0$ der Fehler von f'_{H^+} unendlich groß ist, unbegründet, da dann f'_{H^+} wegen

$$f'_{H^+} = \frac{X_{H^+} \cdot f'_{H^+}}{X_{H^+}} = \frac{0}{0}$$

sowieso unbestimmt wird und für diesen Fall stets durch Extrapolation ermittelt werden muß.

Abgesehen vom Fehler der Bestimmungsmethode ist es sehr unwahrscheinlich, daß f'_{H^+} unabhängig von X_{Na^+} und X_{H^+} den Wert 1 beibehält, da die interionische Wechselwirkung auf die H^+ wegen deren sehr viel größeren Raumladungsdichte einen noch ausgeprägteren Einfluß haben muß als auf die Na^+-Ionen. Wenn wir also große Abweichungen von f'_{Na^+} gegenüber 1 feststellen, die anerkannt werden, so muß erst recht erwartet werden, daß f'_{H^+} solche Abweichunegn zeigt. Im übrigen liegen sie in derselben Richtung, die man in Analogie zum Verhalten des f_{H^+} in wäßrigen Lösungen erwarten sollte. Da überdies die Dielektrizitätskonstante der Quellschicht gegenüber der des Wassers sicher klein ist ($\varepsilon_{\mathrm{Glas}} \sim 5-8$; $\varepsilon_{H_2O} = 81$), läßt sich voraussehen, daß die in wäßrigen Elektrolytlösungen auftretenden Wechselwirkungen in der Quellschicht des Glases sogar in verstärktem Maße in Erscheinung treten werden.

So bewirkt die Coulomb-Wechselwirkung bei hohen H^+-Konzentrationen, daß der Aktivitätskoeffizient f_{H^+} Werte über 1 annehmen kann [2]. Dies stimmt mit dem von uns gemessenen Verlauf für f'_{H^+} im Glas überein.

Da die Na^+ eine bedeutend geringere Ladungsdichte als die H^+-Ionen aufweisen, wird selbst bei hohen Na^+-Konzentrationen die Na^+-H^+-Wechselwirkung durch die H^+-A^--Coulombenergie überkompensiert, wie unsere Messungen für den Fall $X_{Na^+} \rightarrow 1$ zeigen, für den $f'_{H^+} < 1$ ist.

Auch die große Austauschgeschwindigkeit zwischen H^+ und den H-Atomen des Wassers, die in einem hohen Leitfähigkeitsanteil des H^+ gegenüber den Na^+ in der Quellschicht zum Ausdruck kommt [3], läßt eine besonders starke H^+-H^+-Wechselwirkung erwarten, die bei höheren H^+-Konzentrationen zu f'_{H^+}-Werten über 1 führt.

Die experimentellen Befunde über einen konzentrationsabhängigen H^+-Aktivitätskoeffizienten in der Quellschicht der Elektrode können also nicht auf Meßfehlern beruhen und sind im Einklang mit der Theorie der Coulombschen Wechselwirkung dieser Ionen.

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Dr. h. c. Kurt Schwabe; Dresden, Technische Universität

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ÜBER DEN ALKALIFEHLER DER GLASELEKTRODE*

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In einer früheren Arbeit [1] wurde gezeigt, daß der relative Fehler der von SCHWABE und DAHMS [2] zur Bestimmung der Aktivitätskoeffizienten der Wasserstoffionen (f'_{H^+}) verwendeten Methode dem Molenbruch der Wasserstoffionen (X_{H^+}) umgekehrt proportional ist:

$$\frac{\Delta f'_{H^+}}{f'_{H^+}} = K + \frac{k}{X_{H^+}} \tag{1}$$

wobei K und k den relativen Fehler der radiochemischen Messung und der elektrochemischen Bestimmungsmethode des Alkalifehlers enthält. Die Richtigkeit dieses auf theoretischem Wege abgeleiteten Zusammenhanges wird von SCHWABE [3] nicht bezweifelt, dem Wesen nach sogar bekräftigt: »Es kann bestätigt werden, daß der relative Fehler der Bestimmung von f'_{H^+} — vor allem für kleine Werte von X_{H^+} — nach unserer Methode groß ist.« Auf Grund der Gleichung (1) kann im Falle $X_{H^+} \rightarrow 0$ nur ein einziger mathematischer Schluß gezogen werden:

$$\text{für } X_{H^+} \rightarrow 0 \text{ ist } \lim \frac{\Delta f'_{H^+}}{f'_{H^+}} \rightarrow \infty .$$

Die Meßresultate von SCHWABE und DAHMS werden hochgeschätzt; wir haben sie nur aus dem Gesichtspunkte untersucht, ob sie nicht mit unserer bereits beschriebenen Annahme [4] im Gegensatz stehen, wonach der Aktivitätskoeffizient der Natriumionen in der potentialbestimmenden Oberflächenschicht (f'_{Na^+}) von ihrem Molenbruch abhängt, während f'_{H^+} als konstant betrachtet werden kann. Bezüglich f'_{H^+} kann das Meßgebiet des Alkalifehlers in zwei Teile geteilt werden. Im Gebiet $X_{H^+} > X_{Na^+}$ — wo die Wasserstoffionen auf das Phasengrenzpotential einen größeren Einfluß ausüben — ist der relative Fehler von f'_{H^+} auf Grund Gleichung (1) verhältnismäßig gering.

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* Bemerkung zu der vorangehenden Arbeit von K. SCHWABE.

Wir haben auf grund graphischer Auswertung der in Abb. 1 [2] dargestellten Meßdaten, ferner aus der durch die Autoren für das früher beschriebene [5] radiochemische Verfahren angegebenen Fehlergrenze von ±5% den Schluß gezogen, daß im Intervall $X_{H^+} > X_{Na^+}$ die eventuelle Änderung von f'_{H^+} innerhalb der Fehlergrenze liegt.

Es ist bekannt, daß sich mit der Abnahme von X_{H^+} der Einfluß der eventuellen Änderung von f'_{H^+} auf das Phasengrenzpotential verringert. Wenn man daher im Gebiet $X_{H^+} < X_{Na^+}$ von dem rasch zunehmenden Fehler der Bestimmung von f'_{H^+} absehen würde, könnte durch Einführung der vereinfachenden Bedingung $f'_{H^+} = 1$ in der Berechnung des Phasengrenzpotentials kein wesentlicher Fehler begangen werden. Aus dem Gesagten kann unserer Ansicht nach der Schluß gezogen werden, daß die Meßergebnisse von SCHWABE und DAHMS [2] nicht im Gegensatz mit der Annahme $f'_{H^+} = 1$ stehen, sondern vielmehr die Richtigkeit dieser Annahme in dem für das Phasengrenzpotential wesentlichen Intervall ($X_{H^+} > X_{Na^+}$) — unabhängig von der unterschiedlichen Bewertung des relativen Fehlers der Meßungen — auch experimentell unterstützen.

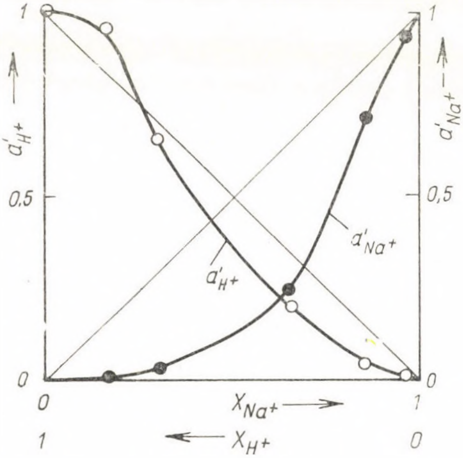

Abb. 1. Zusammenhang zwischen Molenbrüchen und Aktivitäten nach SCHWABE und DAHMS [2]. Die von uns eingezeichneten Geraden entsprechen einem konstanten Aktivitätskoeffizienten

Die entscheidende Annahme zur Deutung des Alkalifehlers [4], wonach f'_{Na^+} sich mit X_{Na^+} wesentlich ändert — da X_{Na^+} unmittelbar bestimmt werden kann, wird durch die Angaben von SCHWABE und DAHMS (Abb. 1) ohne Zweifel im ganzen Meßintervall bestätigt. Die Behauptung [3], »Wenn wir also große Abweichungen von f'_{Na^+} gegenüber 1 feststellen, die anerkannt werden, so muß erst recht erwartet werden, daß f'_{H^+} solche Abweichungen zeigt«, scheint mit den eigenen Meßergebnissen von SCHWABE im Widerspruch zu stehen (vgl. Abb. 1), da die angegebene Änderung von f'_{H^+} (abgesehen von der Frage der Fehlergrenze) wesentlich geringer als die von f'_{Na^+} ist.

Von SCHWABE und DAHMS [2] wurden die Hypothesen mehrerer Autoren [6, 4] diskutiert. Dabei fehlt aber aus ihrer angeführten Arbeit bedauerlicherweise jegliche, zumindest qualitative Information über den Fehler der Bestimmung der Aktivitätskoeffizienten. Wir sind der Ansicht, daß in der diskutierten Frage keine Meinungsverschiedenheit enststanden wäre, wenn die in Frage stehenden Angaben entsprechend erläutert worden wären — wie dies in der vorangehenden Arbeit von SCHWABE der Fall war. Wir möchten betonen, daß wir die hoch eingeschätzten Untersuchungen von SCHWABE und Mitarbeitern nur in bezug auf die Bewertung der früheren Grundannahmen zu ergänzen wünschten und uns in der Klärung der Meinungsverschiedenheit nicht auf unsere eigenen Erfahrungen [1, 4, 7, 8] stützten.

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DETERMINATION OF THE STABILITY CONSTANTS OF $\mathrm{MA}_n\mathrm{B}_{N-n}$ TYPE MIXED LIGAND COMPLEXES

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The great importance of complexes containing different ligands (mixed ligand complexes) is evident, since the formation of this type is always possible when at least two different ligands are present in a given solution.

The present paper gives a general description of systems containing complexes of the type MA_nB_{N-n}. N is either the maximum or the characteristic coordination number. Thus, in these systems the number of coordination places occupied by the two different ligands is always the same in each complex, and it is equal to N. There are two possibilities for such complexes to be formed. First, when MA_nB_{N-n} complexes are formed by the reaction of MA_N and MB_N, and the dissociation of MA_N and MB_N can be neglected under certain given conditions. In this case there is no free ligand *(A* and *B)* in the system. Secondly, when the concentration of the free ligand exceeds a certain (not necessarily equal) limit both for A and B in the given system, and so the coordinative saturation of the complexes in the compound is ensured. We shall deal with the two cases separately.

Systems containing no free ligands

In case of certain metal ions the stability of a complex with less than maximum coordination number (as a rule equal to the valence) is markedly greater than that of complexes with greater or less coordination number. *E.g.*, mercury(II) complexes show this behaviour [1].

Consequently, in a solution of $\mathrm{Hg}A_2$ the concentrations of the dissociation products (Hg^{2+}, $\mathrm{Hg}A^+$, A^-) as well as that of the complexes with greater coordination number ($\mathrm{Hg}A_3^-$, $\mathrm{Hg}A_4^{2-}$) are negligibly small. Therefore, in a solution containing $\mathrm{Hg}A_2$ and $\mathrm{Hg}B_2$ the following reaction takes place exclusively:

$$\mathrm{Hg}A_2 + \mathrm{Hg}B_2 = 2\,\mathrm{Hg}AB\,.$$

Such systems, containing one mixed ligand complex only, can be treated in a simple manner. Extraction (**Marcus** [2]) and spectrophotometric methods

(Spiro and Hume [3]; Beck and Gaizer [4]) have been developed for their study, and the equilibrium constants of different mercury(II) halide mixed complexes have been determined. In the system $MA_3 - MB_3$ evidently two mixed complexes are formed, and the system can be characterized by two equilibrium constants. Gaizer and Beck's method [5] may be applied just in case of such systems, and equilibria in the system $BiCl_3 - BiI_3$ have been studied.

In general, the system $MA_N - MB_N$ can be characterized by $N-1$ equilibria of the following type:

$$MA_{i-1}B_{j+1} + MA_{i+1}B_{j-1} = 2\,MA_iB_j \quad (i+j=N) \tag{1}$$

Introducing $MA_iB_j = c_i$, the equilibrium constant of (1) is

$$K_i = \frac{c}{c_{i-1} \cdot c_{i+1}} \,. \tag{2}$$

After rearrangement:

$$\frac{c_{i+1}}{c_i} = \frac{1}{K_i} \frac{c_i}{c_{i-1}} \,. \tag{3}$$

Balances referred to the ligands are:

$$C_A = \sum_{i=0}^{N} \frac{i}{N} c_i \tag{4}$$

and

$$C_B = \sum_{i=0}^{N} \frac{N-i}{N} c_i \,. \tag{5}$$

C_A and C_B are equal to the concentrations MA_N and MB_N, respectively, introduced *originally* to the system.

Denoting C_A/C_B by R:

$$\frac{C_A}{C_B} = R = \frac{\sum_0^N i\,c_i}{\sum_0^N (N-i)\,c_{N-i}} = \frac{\sum_0^N i\,\frac{c_i}{c_0}}{\sum_0^N (N-i)\,\frac{c_i}{c_0}} \tag{6}$$

Let us denote c_1/c_0 by r; then Eq. (3) gives the following ratio for the concentrations of neighbouring complexes:

$$\frac{c_{i+1}}{c_i} = \frac{r}{K_1 \cdot K_2 \ldots K_i} \,. \tag{7}$$

In balance (6) the term c_i/c_0 is found. By means of Eq. (7), this may be expressed as follows:

$$\frac{c_i}{c_0} = \frac{r^i}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}} . \tag{8}$$

Substituting Eq. (8) into (6), we have:

$$R = \frac{\sum\limits_{i=0}^{N} \dfrac{i\, r^i}{K_1^{i-1} \cdot K_2^{i-2} \ldots K_{i-1}}}{\sum\limits_{i=0}^{N} \dfrac{(N-i)\, r^i}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}}} . \tag{9}$$

That is, in the knowledge of r as a function of R, $N-1$ K_i equilibrium constants can be calculated. It is readily seen that functions analogous to Eq. (9) may be obtained which are useful to calculate changes in the concentrations of any of two neighbouring complexes, or even of any two complexes as the functions of R and the equilibrium constants. Among these, the expression containing $c_N/c_0 = r_N$, *i.e.* the ratio of the actual concentration of two "parent complexes" (MA_N and MB_N), is of special importance. From Eq. (8), it can be written:

$$\frac{c_N}{c_0} = \frac{r^N}{K_1^{N-1} K_2^{N-2} \ldots K_{N-1}} = r_N . \tag{10}$$

Furthermore

$$r = \sqrt[N]{K_1^{N-1} K_2^{N-2} \ldots K_{N-1} \cdot r_N} .$$

Thus Eq. (9) is transformed into the expression:

$$R = \frac{\sum\limits_{i=0}^{N} \dfrac{i}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}} (K_1^{N-1} K_2^{N-2} \ldots K_{N-1})^{\frac{i}{N}} r_N^{\frac{i}{N}}}{\sum\limits_{i=0}^{N} \dfrac{N-i}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}} (K_1^{N-1} K_2^{N-2} \ldots K_{N-1})^{\frac{i}{N}} r_N^{\frac{i}{N}}} . \tag{11}$$

Introducing

$$\varkappa_i = \frac{(K_1^{N-1} K_2^{N-2} \ldots K_{N-1})^{\frac{i}{N}}}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}}$$

and

$$\varrho_N = \sqrt[N]{r_N} .$$

Eq. (11) may be written in the following form:

$$R = \frac{\sum_{0}^{N} i\varkappa_i \varrho_N^i}{\sum_{0}^{N} (N-i)\, \varkappa_i \varrho_N^i}\,. \tag{12}$$

If K_i is known, the values of K_i may be calculated from the following expressions:

$$N = 2: \quad K_1 = \varkappa_1^2$$

$$N = 3: \quad K_1 = \frac{\varkappa_1^2}{2}\,;\; K_2 = \frac{\varkappa_2^2}{1}$$

$$N = 4: \quad K_1 = \frac{\varkappa_1^2}{\varkappa_2}\,;\; K_2 = \frac{\varkappa_2^2}{\varkappa_1 \varkappa_3}\,;\; K_3 = \frac{\varkappa_3^2}{\varkappa_2}\,.$$

It is obvious that in the range $0 < R < \infty$ the mole fraction of each MA_iB_{N-i} complex ($i \neq 0$) changes according to a maximum curve as a function of R. It is easy to point out that the mole fraction of the complex MA_nB_{N-n} has a maximum when $R = n/(N-n)$. The mole fraction can be expressed by the following equation:

$$\alpha_n = \frac{\dfrac{c_n}{c_0}}{\sum_{0}^{N} \dfrac{c_i}{c_0}} = \frac{\dfrac{1}{K_1^{n-1} \cdot K_2^{n-2} \ldots K_{n-1}}\, r^n}{\sum_{0}^{N} \dfrac{1}{K_1^{i-1} K_2^{i-2} \ldots K_{i-1}} \cdot r_i} \tag{13}$$

or in short form:

$$\alpha_n = \frac{\pi_n r^n}{\sum_{0}^{N} \pi_i r^i}\,. \tag{13a}$$

It is obvious that $d\alpha_n/dr = 0$, if

$$\sum_{0}^{N} (n-i)\, \pi_i r^i = 0 \tag{14}$$

A simple rearrangement and reduction of the expression

$$R = \frac{n}{N-n} = \frac{\sum_{0}^{N} i\pi_i r^i}{\sum_{0}^{N} (N-i)\pi_i r^i}$$

results in the same equation. Since Equation (14) has only one positive root (it contains one change of sign), in case of $\alpha_n = \max.$, $R = n/(N-n)$. Thus, the places of maxima do not depend on the equilibrium constants, but naturally the height and shape of α_i versus R curves, are influenced by them. Being all the equilibria constants in question dimensionless quantities, the distribution of the mole fractions of the simple complexes is independent of the absolute value of C_A and C_B.

Systems containing free ligands

In a system containing M central ion and A ligand, if $[A]$ exceeds a certain $[A]_k$ limit, the solution contains only one MA_N complex ion, or more precisely, the concentrations of the others (MA_i; $i < N$) are negligible. Similarly, in a system containing M central ion and B ligand, if $[B] > [B]_k$, MB_N is the only complex ion present. Obviously, in systems containing M central ion as well as both ligands A and B, only complexes of MA_iB_{N-i} composition can exist, supposed that $[A] > [A]_k$ and $[B] > [B]_k$. The distribution of these complexes is determined by the ratio of $[A]/[B]$ and by the series of respective equilibrium constants.

Formation of the complex MA_iB_{N-i} is described by Eq. (15):

$$MA_{i-1}B_{N-i+1} + A \rightleftarrows MA_i B_{N-i} + B\,. \tag{15}$$

Denoting the concentration of MA_iB_{N-i} by c_i, we get:

$$K'_i = \frac{c_i\,[B]}{c_{i-1}\,[A]} \quad (i = 1, 2 \ldots N)\,. \tag{16}$$

Denoting $[A]/[B]$ by x, on the basis of Eq. (16) it follows:

$$\frac{c_1}{c_0} = K'_1\,x = \varkappa'_1\,x$$

$$\vdots$$

$$\frac{c_i}{c_0} K'_1 \ldots K'_1 \cdot x^i = \varkappa'_1\,x^i$$

$$\vdots$$

$$\frac{c_N}{c_0} = K'_1 \ldots K'_N \cdot x^N = \varkappa'_N\,x^N \tag{17}$$

$\varkappa'_N$ is the quotient of complex products (β_N^A and β_N^B) characterizing the overall dissociation of complexes MA_N and MB_N:

$$\varkappa'_N = \frac{[MA_N][B]^N}{[MB_N][A]^N} = \frac{[MA_N]}{[M][A]^N} \cdot \frac{[M][B]^N}{[MB_N]} = \frac{\beta_N^A}{\beta_N^B}. \tag{18}$$

The total metal ion concentration is:

$$C_M = \sum_0^N c_i = c_0 \sum_0^N \frac{c_i}{c_0} = c_0 \sum_0^N \varkappa'_1 x^i \qquad (\varkappa'_0 = 1). \tag{19}$$

The concentration of any chosen complex (c_n) will be:

$$c_n = \frac{\varkappa'_n x^n}{\sum\limits_0^N \varkappa'_i x^i} \cdot C_M. \tag{20}$$

It follows from Eq. (20) that if the change of the concentration of any complex is known as the function of x, the values of N number of $\varkappa'_i$ constants can be readily calculated. From the point of view of experimental possibilities, the method of calculation using the concentration changes of the two "parent complexes" MA_N and MB_N, is of special importance.

The following considerations afford a further possibility of calculation and determination. Balances for A and B are:

$$C'_A = [A] + \sum_0^N i\, c_i = [A] + C_A = [A] + \frac{\sum\limits_0^N i \varkappa'_i x^i}{\sum\limits_0^N \varkappa'_i x^i} C_M \tag{21}$$

$$C'_B = [B] + \sum_0^N (N-i)\, c_i = [B] + C_B = [B] + \frac{\sum\limits_0^N (N-i) \varkappa'_i x^i}{\sum\limits_0^N \varkappa'_i x^i} C_M. \tag{22}$$

The mean coordination numbers of the ligands A and B are:

$$\bar{n}_A = \frac{\sum\limits_0^N i \varkappa'_1 x^i}{\sum\limits_0^N \varkappa'_i x^i} = N - \bar{n}_B$$

$$\bar{n}_B = \frac{\sum\limits_{0}^{N} (N-i)\,\varkappa'_i\,x^i}{\sum\limits_{0}^{N} \varkappa'_i\,x^i} = N - \bar{n}_A$$

$$C'_A = [A] + \bar{n}_A \cdot C_M \tag{23}$$

$$C'_B = [B] + \bar{n}_B \cdot C_M. \tag{24}$$

In the range $0 < x < \infty$, the mole fractions of the two parent complexes obviously change monotonously, and that of the mixed complexes according to a maximum curve, as a function of x. The mole fraction of the n-th complex (α_n) is:

$$\alpha_n = \frac{\varkappa'_n\,x^i}{\sum \varkappa'_i\,x^i}. \tag{25}$$

After differentiation we have:

$$\sum (n-i)\,\varkappa'_i\,x_n^i = 0. \tag{26}$$

This is obviously the same as:

$$n_A = \frac{C_A}{C_M} = n. \tag{27}$$

Thus, the mole fraction of the complex MA_nB_{N-n} has a maximum when $x = x_n$.

If the number of mixed complexes is $N-1$, and the value of x_n is known for each mixed complex, we have $N-1$ expressions to determine N number of unknown complexes. Considering, however, that according to Eq. (18) $\varkappa'_N = \beta_N^A/\beta_N^B$, if β_N^A and β_N^B are known from independent measurements, Eq. (26) also makes possible the determination of the equilibrium constants. The great advantage of this method is that it does not require the knowledge of the free ligand concentrations, because by Eq.-s (23), (24) and (27) they can directly be calculated from the total concentrations belonging to the maximum mole fractions.

Chemical considerations

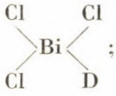
The method suggested requires the knowledge of the concentration of one of the series of mixed or parent complexes as a function of R and x, resp. Experimentally, it seems to be easier to determine the concentration of the parent complexes. Namely, any of the characteristic properties of the two parent complexes can be simply determined, because it is easy to convert the total amount of the central ion into anyone of the coordinatively saturated parent complexes. In general, the mole fraction of anyone of the mixed complexes is much smaller than 1, even at the maximum position, therefore the characteristic properties of these species cannot be determined directly. That is the reason why the method which requires only the knowledge of the position of the maximum mole fraction values of the mixed ligand complexes is considered to have special importance.

As a matter of course, the calculation methods given are suited to use the data of "finger-print" experimental procedures. As the most important of such procedures, Raman spectroscopy may be mentioned [6]. Evidently, the formation of the mixed ligand complexes of the same "coordination level" [3] is fully general in case of systems containing free ligand. The existence of such type of mixed complexes in the system containing no free ligands is mostly restricted to the electrically neutral complexes. The following cases seem to be the most important:

(*i*) Monodentate ligands, having one negative charge (MA_nB_{N-n}, M^{m+}, $m = N$).

(*ii*) Bidentate ligands, having one negative charge (MA_nB_{N-n}, M^{m+}, $m = N/2$).

Examples for (*i*) have been given in this paper. It must be added that although in the calculation of the equilibrium constants the participation of the solvent in the coordination may be rightfully disregarded, in the formulation of a given species the donor properties of the solvent have to be taken into account. E.g., the structure of the $BiCl_iI_{3-i}$ species in dioxan is probably as follows:



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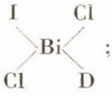

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There are only a few examples for (*ii*). The work of JANSSEN [7], however, shows that a great number of such complexes may exist. Work with any pair of the following ligands seems to be especially promising: 8-hydroxyquinoline (and derivatives), dimethylglyoxime (and analogous compounds), acetylacetone (and analogous compounds), N-dialkyldithiocarbamic acids. With bivalent metal ions of coordination number 4 only one, with trivalent central ions of coordination number 6 two mixed ligand complexes exist. In these cases the methods developed earlier may also be used.

SUMMARY

Two different systems of mixed ligand complexes of the composition MA_nB_{N-n} can be distinguished: systems in which the concentration of the free ligands is negligible and in which these concentrations are commensurable with, or even larger than the concentrations of the complexes. Different methods are discussed to calculate the equilibrium constants. One of the methods does not require the knowledge of the concentration of the complexes, only the concentration ratios of the free ligands at the maximum concentration of each mixed ligand complex are needed.

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VERGLEICHENDE UNTERSUCHUNGEN ÜBER DIE MIT DER STUFENFILTERMETHODE AUFGESTELLTE SCHWÄRZUNGSKURVE*

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Einleitung

Auf der III. Rumänischen Spektroskopischen Konferenz in Bukarest im Dezember 1964 beschäftigte sich einer von uns [1] mit den prinzipiellen Problemen der zur Aufstellung der Schwärzungskurve vorgeschlagenen Methoden bzw. mit den Vorteilen und Nachteilen der verschiedenen Verfahren. Auf derselben Konferenz wurde auch ein Beweis des exakten Charakters einer zur äußerst einfachen und genügend genauen Aufstellung der Schwärzungskurve dienenden Methode vorgelegt. Diese Methode fußt auf der Bereitung einer Spektralaufnahmeserie bei variierten Belichtungszeiten, unter Anwendung einer zweistufigen strahlungsschwächenden Einrichtung (z. B. eines Zweistufenfilters). Wie es bewiesen wurde, kann in solchen Fällen der Schwarzschild-Effekt vermieden werden.

Logarithmischer Filter

Durch Verwendung des von Z. NAGY und Mitarbeitern [2] konstruierten und uns zur Verfügung gestellten Stufenfilters mit variierbarer Filterkonstante konnten wir bei solchen Untersuchungen, in welchen die Messungen bei verschiedenen Wellenlängen durchgeführt werden, immer den Stufenfilterteil mit entsprechender Filterkonstante in den Strahlungsgang stellen. Der mittlere, aus einer Quarzplatte bereitete und vollkommen durchlässige Teil dieses Dreistufenfilters berührt zwei Stufen, deren Durchlässigkeiten in einer zur Spalte senkrechten Richtung beinahe logarithmisch sind. Demgemäß verändert sich die Schwärzung der Emulsion an dem geraden Teil der Schwärzungskurve in einem fast linearen Masse. Mittels einer Mikrometerschraube kann man die Stufe geringerer Durchlässigkeit getrennt, die Stufen von mittlerer und voller Durchlässigkeit hingegen gemeinsam in einer zur Spalte senkrechten Richtung einstellen.

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*Vorgetragen an der III. Tschechoslowakischen Spektroskopischen Konferenz, Mariánské Lázně, 28. Sept. 1965.

Eichung des logarithmischen Filters

Die zu unseren Messungen benötigten Schwärzungsdifferenzen von etwa 0,20 entsprechenden Filterstellungen wurden für die verschiedenen Wellenlängen mittels Vorversuche festgestellt. Dann wurde die Eichung der Filterkonstante (ΔY^l_m) für die ausgewählten Wellenlängen durch Vergleich mit einem Zweistufenfilter genau bekannter Filterkonstante (ΔY^z_m) durchgeführt:

$$\Delta Y^l_m = \frac{\overline{\Delta S^l}}{\overline{\Delta S^z}} \cdot \Delta Y^z_m$$

wobei ΔS die auf dem linearen Abschnitt der Schwärzungskurve bei zwei Stufen der gegebenen Spektrallinien gemessene durchschnittliche Schwärzungsdifferenz bezeichnet, während sich der Index l auf den Filter mit einer in logarithmischem Maße variierbarer Filterkonstante (d. h. auf den eine linear

Tabelle I

Filterkonstantenwerte des Dreistufenfilters veränderlicher Filterkonstanten bei verschiedenen Wellenlängen

λ (nm)	ΔY_{I}	ΔY_{II}
227,84	0,287	0,351
243,36	0,240	0,280
263,03	0,220	0,257
282,13	0,197	0,253
304,50	0,180	0,241
319,71	0,170	0,204
328,76	0,173	0,219
335,91	0,167	0,207
340,96	0,156	0,221
348,59	0,128	0,200
355,15	0,157	0,191
358,79	0,127	0,166
366,41	0,130	0,172
373,92	0,164	0,201
376,95	0,107	0,193
397,37	0,148	0,183
445,90	0,127	0,204
471,44	0,137	0,193
510,00	0,101	0,178
514,28	0,105	0,187

veränderliche Schwärzung hervorrufenden Filter), und Index *z* auf den Zweistufenfilter mit bekannter Filterkonstante bezieht. Die bei einer geeigneten Stellung der beiden Stufen des Filters für verschiedene Wellenlängen erhaltenen Werte der Filterkonstante sind in Tab. I zusammengefaßt.

Sichtbarer Wellenlängenbereich

Im sichtbaren Wellenlängenbereich ist der lineare Abschnitt der Schwärzungskurve und dementsprechend jener der Hilfskurve [3] äußerst kurz. Bei größeren Schwärzungswerten ergibt sich auf dieser Hilfskurve eine starke Rückbiegung zur Abszissenachse (Abb. 1). Die starke Rückbiegung ist offenbar dem zuzuschreiben, daß die sensibilisierte Emulsion in bezug auf sichtbares Licht von geringerer Energie rascher gesättigt wird.

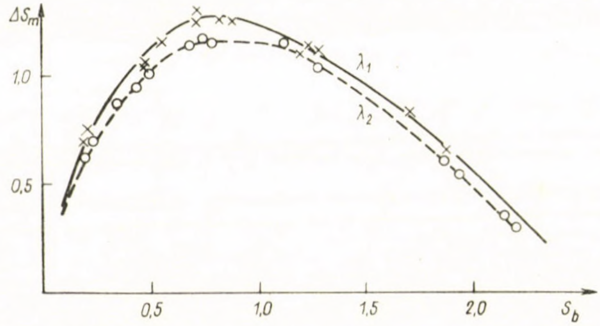

Abb. 1. Abhängigkeit der der Filterkonstante (ΔY_m) entsprechenden Schwärzungsdifferenz (ΔS_m) von den an der geschwächten Filterstufe gemessenen Schwärzungen (S_b) im sichtbaren Wellenlängengebiet

$\lambda_1 = 516{,}86$ nm, $\gamma_1 = 4{,}06$
$\lambda_2 = 558{,}78$ nm, $\gamma_2 = 3{,}74$

Infolge der Kürze des linearen Abschnittes wird die genaue Bestimmung von γ ziemlich erschwert. Überdies besitzen die zu den in kommerziellem Verkehr erhaltbaren Spektrografen gelieferten Zwei- bzw. Mehrstufenfilter für die Wellenlängen über 400 nm schon sehr hohe Filterkonstanten. Für *Orwo rot extrahart* Spektralplatten beträgt γ z. B. um 500 nm den Wert 4 (derselbe Wert ergibt sich für *Kodak B 10* oder *Gevaert Scientia 23 D 56* Platten um 400 nm). Mit dem Zweistufenfilter von 50% Durchlässigkeit ($\Delta Y = 0{,}30$) mißt man in diesem Fall eine Schwärzungsdifferenz von $\Delta S_m = \gamma \cdot \Delta Y_m = 1{,}20$. Bei dieser Wellenlänge ist der untere Grenzwert des linearen Abschnittes der reduzierten Schwärzungskurve 0,25 [4], entsprechend einer Schwärzung von $0{,}25\,\gamma = 1{,}00$, man sollte daher bei den ungeschwächten Stufen eine Schwärzung von $1{,}00 + 1{,}20 = 2{,}20$ messen.

Führt man jedoch die Messung auf einer Linie mit geringerer Schwärzung durch, so fällt die Schwärzung der ungeschwächten Stufe auf den unterexponierten Abschnitt. Auf solche Weise mag es vorkommen, daß es unmöglich ist Schwärzungen entsprechend dem linearen Abschnitt zu messen, d. h. der Wert von γ kann gar nicht bestimmt werden. In diesem Fall wird die Anwendung des oben beschriebenen sogenannten logarithmischen Filters von veränderlicher Durchlässigkeit eine große Hilfe leisten. Im oben erwähnten Fall mit einer Filterkonstante von 0,10 beträgt z. B. der Wert $\Delta S_m = \gamma \cdot \Delta Y_m = 0{,}40$, d. h. eine Anzahl von Aufnahmen kann zwischen den Grenzwerten $S_a = 1{,}00$ und $S_b = 1{,}40$ bzw. $S_a = 1{,}60$ und $S_b = 2{,}00$ bereitet werden, somit stehen genügend viele Angaben zur genauen Bestimmung von γ zur Verfügung.

Messung hoher Schwärzungen

Bei der genauen Messung hoher Schwärzungen (über etwa 1,5) ergeben sich Schwierigkeiten, weil die Skaleneinleitung des Spektrallinien-Photometers in diesem Bereich schon zu eng ist. Zur Überwindung dieser Schwierigkeiten soll man auf dem Photometer unter den gegebenen Versuchsbedingungen (Spaltbreite, Spalthöhe, Schleierwert usw.) jene noch möglich niedrigste Empfindlichkeitsgrenze einstellen, bei welcher der Nullpunkt der Schwärzungsskala noch einstellbar ist. Sodann wird die Stellung der Platte so verändert, daß das Licht von jenem Abschnitt der Spektrallinie ins Photometer gelange, dessen Schwärzung 1,00 beträgt. Daraufhin wird die Empfindlichkeit zur maximalen Stufe umgeschaltet, und der Galvanometerausschlag abgelesen. Die hohen Schwärzungen werden auf dieser Stufe maximaler Empfindlichkeit gemessen. In jedem Fall muß man aber die Differenz der bei zwei verschiedenen Empfindlichkeitsstufen gemessenen Schwärzungen zu den abgelesenen Werten hinzugeben. So ist es möglich, bis zu Schwärzungen von 2,5 mit einer genügenden Genauigkeit zu messen.

Unterexponierte Aufnahmen

Die Steilheit der Schwärzungskurve soll durch die Schwärzungswerte auf dem linearem Abschnitt bestimmt werden. Wenn jedoch nur eine unterexponierte Aufnahme zur Verfügung steht, die Spektren aber mit einem Stufenfilter bekannter Filterkonstante bereitet wurden, so ist die Bestimmung des γ-Wertes mittels l-Transformation [5] doch möglich. Dazu muß man den Wert von k auf der betreffenden Spektrallinie kennen. Dieser ist aber bei Anwendung der l-Transformation schon im voraus bekannt. Die Bestimmung erfolgt sodann durch Iteration. Angenommen, daß $\gamma = 1$ ist, so werden die zum Schwärzungspaar S_a, S_b gehörenden transformierten Schwärzungswerte l_a, l_b aus der entsprechenden k-Tabelle [4] entnommen. Nachdem wird die Differenz Δl ermittelt. Falls die Differenz gleich ΔY ist, beträgt der γ-Wert$=1$. Wenn sich aber eine Abweichung ergibt, so werden die Werte S_a, S_b mit den wahrscheinlicherem γ-Wert dividiert, und der Wert von Δl wieder auf die vorangehend beschriebene Weise bestimmt. Die Iteration wird so lange wiederholt, bis die Gleichheit $\Delta l = \Delta Y_m$ erreicht wird, was sich nur im Falle von Anwendung des richtigen γ-Wertes ergibt. Mit gewisser Übung kann dies in einigen Schritten leicht erreicht werden.

Nachbarlinien

Bei den sogenannten extrahart Platten ist im Wellenlängenbereich 240—320 nm der Wert von γ wesentlich konstant, er vermindert sich bei etwa 319—320 nm um ungef. 0,1 Einheit, dann erhöht er sich stufenweise bis etwa 450 nm. Bei Platten, die auf sichtbares Licht sensibilisiert wurden, erfolgt diese Erhöhung bis etwa 510 nm, dann wird eine Verminderung bei höheren Wellenlängen beobachtet. Der γ-Wert der Emulsion *Kodak SA 3* (Typ rapid) ist annähernd unabhängig von der Wellenlänge.

Jene Tatsache, wonach der Wert von γ im mittleren ultravioletten Spektralbereich im allgemeinen konstant ist [6], wird bei Rutinanalysen in der Praxis oft auf solche Weise verwendet, daß man auch bei anderen Linien dieses Bereiches mit dem für eine einzige Linie bestimmten γ-Wert rechnet. Bei Spektrallinien geringer Intensität werden die zur Aufstellung der Schwärzungskurve nötigen γ-Werte oft aus den Schwärzungswerten der intensiveren Nachbarlinien bestimmt. Bei nahestehenden Linien wird dieses Verfahren auch bei längeren Wellenlängen angewendet, bei welchen sich γ mit der Wellenlänge beträchtlich erhöht, oder man bestimmt den γ-Wert einer gegebenen Linie durch Interpolation.

Es wurde untersucht, inwiefern dieses Verfahren als richtig betrachtet werden darf. In Tab. II wurden die in zwei Wellenlängenbereichen erhaltenen γ-Werte im Falle des Nickelspektrums für zahlreiche Nickelnachbarlinien zusammengestellt. Wie die Angaben zeigen, überschreiten die im mittleren ultravioletten Spektralbereich beobachteten Fluktuationen des γ-Wertes die in der praktischen Spektralanalyse gestatteten Grenzen im allgemeinen nicht. Um 350 nm können jedoch schon wesentlich größere Abweichungen vorkommen. Daher — besonders bei Analysen erhöhter Genauigkeit — soll man die Gradation für jede Analysenlinie unabhängig voneinander bestimmen.

Tabelle II

γ-Werte von benachbarten Nickellinien in verschiedenen Wellenlängenbereichen

λ (nm)	γ	λ (nm)	γ
298,17	1,24	354,82	1,76
298,41	1,23	355,15	1,56
299,26	1,22	356,18	1,62
299,45	1,20	356,69	1,68
300,25	1,13	357,19	1,75
300,36	1,16	357,68	1,76
301,20	1,17	358,79	1,70
301,91	1,26		
303,79	1,20		
305,08	1,15	366,41	1,89
305,43	1,15	367,41	1,99
305,76	1,10	368,34	1,93
306,46	1,20		
309,71	1,22		
309,91	1,22		
310,55	1,23		
311,41	1,24		
313,41	1,14		
321,41	1,19		
321,78	1,19		
322,17	1,21		
322,30	1,21		
323,30	1,21		
323,47	1,26		

Untersuchung von Emulsionen

Die γ-Werte 17 verschiedener Spektralplattentypen bei unterschiedlichen Wellenlängen sind in den Tab. III—XX zusammengefaßt [7]. Wenn man die mit dem *PGS 2* Gitterspektrographen (Tab. XXI) bei den gleichen Wellenlängen an den gleichen Spektralplatten *(Orwo blau extrahart)* unter derselben Entwicklungsbedingungen erhaltenen γ-Werte miteinander vergleicht, so findet man bei den mit dem Gitterspektrographen bereiteten Aufnahmen für alle Spektrallinien höhere γ-Werte. Die Untersuchung dieser Erscheinung ist im Gange.

Tabelle III

Orwo blau rapid

λ (nm)	γ	λ (nm)	γ_P
251,09	1,06	251,09	1,17
313,41	1,21	313,41	1,28
337,20	1,16		
357,19	1,76		
380,71	1,84	380,71	1,90
440,15	1,96	440,15	2,08

Tabelle IV

Orwo blau extrahart

λ (nm)	γ	λ (nm)	γ_P
227,87	0,62	227,87	0,77
243,36	1,07		
263,03	1,17	263,03	1,19
282,13	1,10		
304,50	1,12	304,50	1,14
320,21	1,01	320,21	1,09
328,70	1,15		
340,96	1,45	358,79	1,88
373,92	2,46		
397,37	2,80	397,37	2,95
440,15	3,21	440,15	3,40

Tabelle V

Orwo blau extrahart

λ (nm)	γ	λ (nm)	γ_P
227,73	0,49	227,73	0,52
282,13	0,74	261,01	0,89
305,08	0,74	305,08	0,86
323,47	0,87	323,47	0,90
346,75	1,26	346,75	1,30
376,41	1,64		
387,17	1,88		
397,36	1,90	397,36	2,11
440,15	2,53	440,15	2,57
475,21	2,61	475,21	3,06

Tabelle VI

Agfa blau rapid (1961)

λ (nm)	γ	λ (nm)	γ_P
247,31	0,89	247,31	1,00
298,41	0,90	298,41	1,01
311,41	0,93		
354,82	1,20	354,82	1,38
367,41	1,31		
378,35	1,40	378,35	1,51
440,15	1,63	440,15	1,77
471,44	1,56	471,44	1,98

Tabelle VII

Agfa blau rapid (1962)

λ (nm)	γ	λ (nm)	γ_P
243,74	0,70	243,74	0,79
294,39	0,80	294,39	0,83
313,41	0,82	313,41	0,96
336,96	0,85		
357,19	1,03	357,19	1,10
380,71	1,55	380,71	1,64

Tabelle VIII

Agfa blau hart (1960)

λ (nm)	γ	λ (nm)	γ_P
227,73	0,37	227,73	0,38
263,03	1,01		
282,13	1,03	282,13	1,13
304,50	1,17		
323,47	1,23	323,47	1,28
346,75	1,44		
367,41	1,65	367,41	1,89
383.17	1,83		
440,15	2,16	440,15	2,18
471,44	2,17	471,44	2,38

Tabelle IX

Agfa blau extrahart (1960)

λ (nm)	γ
227,64	0,58
261,14	1,10
279,87	1,12
299,11	1,29
319,56	1,09
363,49	2,15

Tabelle X

Kodak B 10

λ (nm)	γ	λ (nm)	γ_P
227,64	1,21	227,64	1,22
263,03	1,75	263,03	1,78
283,46	1,39		
312,93	1,70	312,93	1,72
328,27	1,64		
355,35	2,73	355,35	2,84
373,92	3,52		
397,37	4,17	397,37	4,47

Tabelle XI

Kodak SA 1

λ (nm)	γ	λ (nm)	γ_P
263,03	1,43	263,03	1,51
298,41	1,07	298,41	1,22
319,56	1,10	319,56	1,32
356,18	2,07		
374,90	2,30	374,90	2,48
428,80	2,63	428,80	2,82

Tabelle XII

Kodak SA 3

λ (nm)	γ	λ (nm)	γ_P
263,03	0,97	243,74	0,94
282,52	0,88	263,03	1,10
299,17	0,90	299,17	0,93
320,04	0,84		
339,62	1,05	339,62	1,17
355,35	1,10		
384,96	1,26	384,96	1,53
406,44	1,21	406,44	1,36
442,70	1,11	442,70	1,20

Tabelle XIII

Ilford N 30 ordinary

λ (nm)	γ	λ (nm)	γ_P
244,18	1,00	230,78	0,74
263,03	1,11		
299,11	0,97	282,52	0,98
320,04	0,99	320,04	1,08
335,91	1,23		
358,79	2,08		
384,96	2,34	384,96	2,66

Tabelle XIV

Ilford N 40

λ (nm)	γ	λ (nm)	γ_P
243,36	1,25	243,36	1,30
263,03	1,24		
298,41	1,22	298,41	1,36
319,71	1,10	319,71	1,19
332,23	1,26	332,23	1,44
358,79	1,99	358,79	2,19

Tabelle XV

Ilford N 50

λ (nm)	γ	λ (nm)	γ_P
227,87	0,77	227,87	0,99
343,36	1,28		
261,01	1,31	261,01	1,51
280,31	1,23		
298,41	1,11	298,41	1,25
319,71	1,01	319,71	1,28
340,96	1,52		
357,68	2,49		
383,17	2,67		
397,36	3,10	397,36	3,24
445,90	3,76	445,90	4,58

Tabelle XVI

Gevaert Scientia 23 D 56

λ (nm)	γ	λ (nm)	γ_P
243,36	2,04	243,36	2,34
263,03	2,05		
280,31	2,04	280,31	2,21
303,19	2,06		
319,71	1,98	319,71	2,05
339,62	2,08		
357,68	3,52	357,68	3,66
383,17	3,63		
397,37	4,06	397,37	4,12
440,15	4,25	440,15	5,30

Tabelle XVII

Orwo gelb extrahart

λ (nm)	γ	λ (nm)	γ_P
298,41	0,96	298,41	0,98
323,47	1,09	323,47	1,16
351,86	1,71		
376,95	2,45	376,95	2,62
440,15	3,30	440,15	3,13
471,44	3,33	471,44	3,52
		514,28	3,64

Tabelle XVIII

Orwo rot extrahart

λ (nm)	γ	λ (nm)	γ_P
304,50	1,08	304,50	1,30
325,07	1,12	325,07	1,29
373,68	2,16	373,68	2,35
440,15	3,10	440,15	3,20
471,44	3,46	471,44	4,19
508,00	3,90	508,00	4,02

Tabelle XIX

Agfa gelb extrahart

λ (nm)	γ	λ (nm)	γ_P
247,31	0,91		
298,41	0,83	298,41	0,85
324,31	0,98	324,31	1,00
350,09	1,50		
376,95	2,08	376,95	2,24
440,15	2,95	440,15	3,11
		471,44	3,05
514,28	3,20	514,28	3,22

Tabelle XX

Agfa rot extrahart

λ (nm)	γ	λ (nm)	γ_P
247,31	1,02		
298,41	0,91	298,41	0,93
324,31	1,01	324,31	1,03
351,86	1,55		
376,95	2,21	376,95	2,40
397,36	2,36	397,36	2,40
440,15	3,10	440,15	3,22
471,44	3,30	471,44	3.30
514,28	3,30	514,28	3,42

Tabelle XXI

γ-Werte bei verschiedenen Wellenlängen
Spektralplatte: Orwo blau extrahart
Spektrograph: PGS 2 Plangitterspektrograph

λ (nm)	γ
299,11	1,41
331,23	1,90
358,79	2,41
376,95	2,80
440,15	2,88

Für die Untersuchung von Filmen wurde die Plattenkassette auf solche Weise umgebaut, daß sie auch als Filmkassette benützt werden konnte. Durch Anwendung von zwei mit Federplatten versehenen Schienen gleicher Länge, d. h. für die Einheftung von Filmstücken von 24 cm Länge wird die genaue Lage des Films auf der fokalen Oberfläche des Spektrographen gesichert. Die γ-Werte für *Orwo* und *Forte* Filme sind in Tab. XXII angegeben. Von diesen beiden Filmtypen sind die Orwo-Filme sehr gut verwendbar, da sie schleierfrei arbeiten, und die Reproduzierbarkeit der Schwärzungen genügend ist.

Tabelle XXII

γ-Werte von Filmen

Orwo Film		Forte Film	
λ (nm)	γ	λ (nm)	γ
243,78	1,32	298,41	0,85
298,41	1,47	308,08	0,81
319,71	1,41	332,23	1,07
332,23	1,63	354,82	1,23
346,95	1,88	373,68	1,32
367,41	2,16		

Reduzierte Schwärzungskurve

Neben der üblichen Darstellung der Schwärzungskurven bereiteten wir auch sogenannte reduzierte Schwärzungskurven, d. h. wir haben auf der Ordinate die mit γ dividierten Schwärzungswerte aufgetragen. Zwecks Erleichterung des Vergleichs wurden die Schwärzungskurven auf solche Weise konstruiert, daß die Verlängerung des linearen Abschnittes durch die Origo

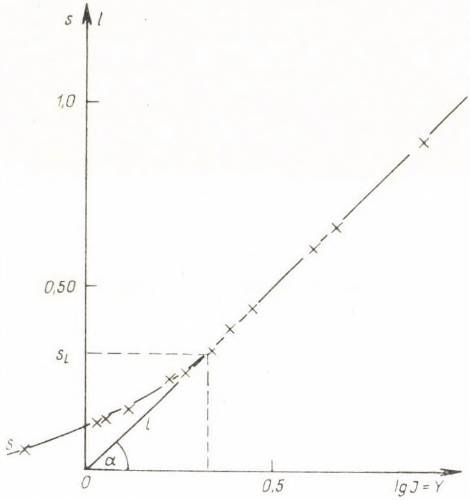

Abb. 2. Aufstellung der reduzierten und transformierten Schwärzungskurven im Falle von Spektralplatten *Orwo blau extrahart* bei 320,21 nm Wellenlänge

$$\gamma = \operatorname{tg} \alpha \,, \quad s_L = \frac{S_L}{\gamma} = k$$

gehe (Abb. 2). Bei solcher Darstellung sind die linearen Abschnitte der reduzierten Schwärzungskurven unabhängig vom Plattentyp und der Wellenlänge miteinander kongruent. Demzufolge zeigen sich im unterexponierten Abschnitt die von γ unabhängigen kennzeichnenden Unterschiede unmittelbar (Abb. 3

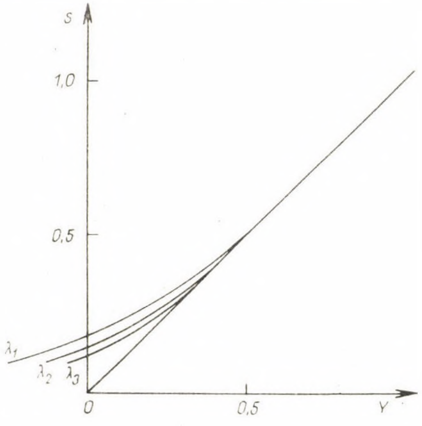

Abb. 3. Reduzierte Schwärzungskurven im Falle von Spektralplatten *Orwo blau ultrahart* bei verschiedenen Wellenlängen

$\lambda_1 = 323{,}47$ nm, $s_E = 0{,}19$, $s_{0{,}10} = 0{,}22$, $k = 0{,}60$
$\lambda_2 = 346{,}75$ nm, $s_E = 0{,}21$, $s_{0{,}10} = 0{,}28$, $k = 0{,}70$
$\lambda_3 = 475{,}21$ nm, $s_E = 0{,}15$, $s_{0{,}10} = 0{,}12$, $k = 0{,}48$

und 4). Den unterexponierten Abschnitt der Schwärzungskurven bzw. der reduzierten Schwärzungskurven kann man mit den folgenden drei Werten kennzeichnen [8]:

a) der Punkt mit dem höchsten Schwärzungswert im unterexponierten Abschnitt ($S_L = \gamma \cdot s_L$, $s_L = k$);

b) der dem Inertiepunkt entsprechende Schwärzungswert ($S_E = \gamma \cdot s_E$). Der Inertiepunkt ergibt sich dort, wo der verlängerte lineare Abschnitt der Schwärzungskurve die Abszisse schneidet. Bei der vorgeschlagenen Darstellungsweise bedeutet dies immer die Origo. Die diesem Punkt entsprechende Schwärzung ist der Schnittpunkt der Schwärzungskurve mit der Ordinate;

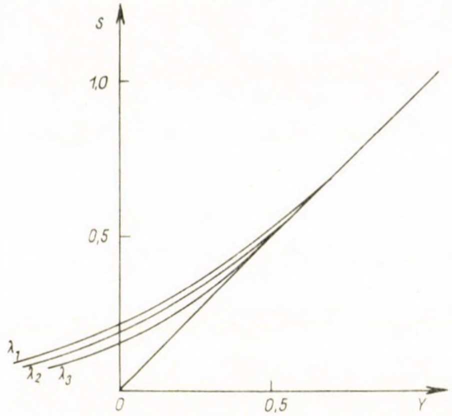

Abb. 4. Reduzierte Schwärzungskurven im Falle von Spektralplatten *Orwo gelb extrahart* bei verschiedenen Wellenlängen

$\lambda_1 = 298{,}41$ nm, $s_E = 0{,}175$, $s_{0,10} = 0{,}195$, $k = 0{,}50$
$\lambda_2 = 351{,}86$ nm, $s_E = 0{,}135$, $s_{0,10} = 0{,}085$, $k = 0{,}41$
$\lambda_3 = 471{,}44$ nm, $s_E = 0{,}12$, $s_{0,10} = 0{,}045$, $k = 0{,}32$

c) anstatt der ungenauen Bestimmung jener Intensität, die der geringsten — mit dem Schleierwert gleichen — Schwärzung des unterexponierten Abschnittes entspricht, ist der dritte Wert der zur Schwärzung 0,10 gehörende log I Wert, von der Origo berechnet ($S_{10} = \gamma \cdot s_{10}$).

Zwischen den oben erwähnten drei Werten, wie dies aus Tab. XXIII hervorgeht, besteht auch bei Emulsionen unterschiedlichen Typs und bei verschiedenen Wellenlängen ein streng monotoner Zusammenhang. Daher kann der unterexponierte Abschnitt mit einer einzigen Angabe, zweckdienlich mit dem k-Wert, während die gesamte Schwärzungskurve mit zwei Angaben (mit k und γ) eindeutig gekennzeichnet werden.

Tabelle XXIII

Drei charakteristische Punkte einiger reduzierter Schwärzungskurven bei verschiedenen Emulsionen

Platte	λ (nm)	s_L	s_E	$s_{0,10}$
Orwo blau rapid	337,20	0,45	0,15	0,13
	357,19	0,55	0,18	—
	380,71	0,37	0,13	0,08
Orwo blau extrahart	260,11	0,37	0,14	—
	282,13	0,34	0,11	0,05
	320,21	0,30	0,11	0,02
	328,70	0,31	0,11	0,03
	335,04	0,31	0,12	0,04
	373,92	0,30	0,10	0,06
Orwo blau ultrahart	323,47	0,60	0,19	0,22
	346,75	0,70	0,21	0,28
	475,21	0,48	0,15	0,12
Kodak B 10	283,46	0,30	0,11	0,02
	328,27	0,30	0,11	0,02
Kodak SA 3	263,03	0,67	0,20	0,23
	282,52	0,57	0,19	0,18
Ilford N 30	263,03	0,30	0,12	0,04
	299,11	0,33	0,13	0,05
	384,96	0,31	0,12	0,05
Ilford N 50	261,01	0,25	0,10	0,00
	298,41	0,40	0,14	0,09
	319,71	0,40	0,15	0,12
	340,96	0,31	0,11	0,03
Gevaert Scientia 23 D 56	263,03	0,20	0,08	—0,04
	280,31	0,20	0,08	—0,04
	303,19	0,25	0,10	0,01
	319,71	0,27	0,10	0,00
	383,17	0,25	0,09	—0,01
Orwo gelb extrahart	298,41	0,50	0,17	0,19
	351,86	0,41	0,13	0,08
	471,44	0,32	0,12	0,04
Orwo rot extrahart	304,50	0,45	0,15	—
	373,68	0,39	0,13	0,12
	440,15	0,32	0,11	0,03
	471,44	0,30	0,10	0,00

Wirkung der Entwicklung

Ablauf und Gradation der Schwärzungskurve hängen bekanntlich von der angewandten Entwicklungsmethode ab. In Tab. XXIV sind die γ-Werte bei 20 °C mit unterschiedlichen Entwicklungsdauern (von 2 bis 12 Minuten) entwickelten Spektralplatten *Orwo blau extrahart* zusammengestellt. Nach Literaturangaben [9] nimmt mit der Verlängerung der Entwicklungsdauer der γ-Wert erst rasch zu, dann — nach einer Entwicklungsdauer von etwa zehn Minuten — nähert er sich einem Grenzwert an, d. h. er verändert sich gemäß einer Sättigungskurve. Nach Literaturangaben [10] erscheint bei gewissen Emulsionen ein starker Schleier schon bei einer zehnminutigen Entwicklungsdauer. Dies haben wir im Falle von *Orwo blau extrahart* Platten nicht beobachtet. Nach Abb. 5 war dagegen bei einer 12minutigen Entwicklungsdauer — ähnlich der anderen angewandten Entwicklungsdauer — der Wert von γ bis 320 nm höher als bei

Tabelle XXIV

γ-Werte bei Veränderung der Entwicklungszeit

t (min)	λ (nm)	γ	t (min)	λ (nm)	γ
2	243,36	0,91	6	243,36	1,21
	298,41	0,86		298,41	1,19
	319,71	0,78		319,71	1,08
	358,79	1,63		358,79	2,08
	376,95	2,28		376,95	2,55
3	243,36	1,00	7	243,36	1,34
	298,41	0,99		298,41	1,35
	319,71	0,96		318,33	1,18
	358,79	1,88		319,71	1,25
	376,94	2,45		376,95	3,06
4	243,36	1,02	8	298,41	0,87
	319,71	0,93		318,33	1,18
	298,41	1,03		331,23	1,51
	358,79	1,87		358,79	2,37
	376,95	2,42		376,95	3,18
5	243,36	1,07	12	243,36	1,65
	282,13	1,10		298,41	1,76
	320,21	1,01		319,71	1,73
	340,96	1,45		358,79	2,26
	373,92	2,46		376,95	2,58

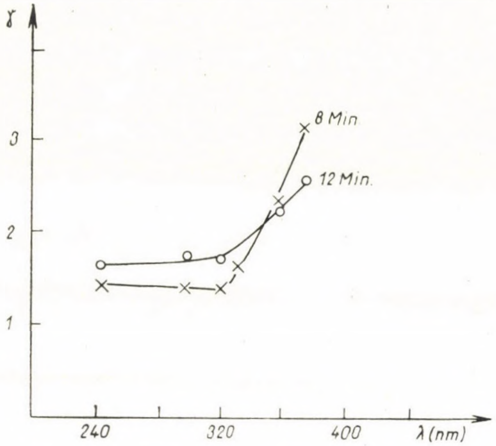

Abb. 5. Abhängigkeit der γ-Werte von der Wellenlänge bei verschiedenen Entwicklungszeiten

einer 8minutigen Entwicklung. Von dieser Wellenlänge an wies aber der γ-Wert ein weniger steiles Erhöhen auf und — in Gegensatz zu den Literaturangaben — war der oben angegebene allgemeine Zusammenhang ungültig, weil wir über 350 nm bei längeren (12minutigen) Entwicklungsdauern geringere γ-Werte erhielten als bei kürzerer Entwicklungsdauer (8minutiger). Mit der Erhöhung der Temperatur nahm der γ-Wert bei allen Wellenlängen eindeutig zu (Tab. XXV).

Neunstufenfilter

Zu den Spektrographen werden im allgemeinen auch mehrstufige (6- bzw. 9stufige) Filter geliefert. Durch Anwendung der mit diesen Stufenfiltern bereiteten Aufnahmen kann man die Schwärzungskurve viel rascher und einfacher aufstellen, falls die entsprechenden Filterkonstanten der Stufen genau bekannt sind. Die Nachteile dieses Verfahrens wurden a. a. O. erörtert [1].

Die Eichung der zu den sowjetischen Spektrographen gelieferten Neunstufenfilter wurde von uns mittels eines *Hilger Uvispek* Spektrophotometers im Wellenlängenbereich 240—670 nm bei 8 verschiedenen Wellenlängen durchgeführt. Im ultravioletten Bereich diente eine Wasserstofflampe als Lichtquelle, im sichtbaren Spektralbereich hingegen eine Wolframlampe. Ein Aufsatz wurde zum Festhalten des Filters und zur Ausschaltung der entsprechenden unverwendeten Filterstufen entwickelt. Die Filterkonstanten sind auf Abb. 6, die bei zwei Wellenlängen mit dem Neunstufenfilter aufgestellten Schwärzungskurven auf Abb. 7 dargestellt. Zum Vergleich bereiteten wir auch Aufnahmen auf denselben Platten mit einem Zweistufenfilter. Nach den

Tabelle XXV

γ-Werte bei Veränderung der Entwicklungstemperatur

T (°C)	λ (nm)	γ
10	243,36	0,93
	298,41	0,87
	319,71	0,80
	358,79	1,63
	376,95	2,26
15	243,36	0,88
	298,41	0,88
	319,71	0,83
	358,79	1,73
	376,95	2,30
20	243,36	1,07
	282,13	1,10
	320,21	1,01
	340,96	1,45
	373,92	2,46
25	243,36	1,33
	298,41	1,31
	319,71	1,20
	358,79	1,97
	376,95	2,57
28	243,36	1,56
	298,41	1,52
	319,71	1,47
	358,79	2,41
	376,95	2,79

Angaben von Tab. XXVI ergaben sich bei den mit dem Neunstufenfilter bereiteten Aufnahmen höhere Werte, als die mit dem Zweistufenfilter erhaltenen. Diese Abweichung kann man nicht dem asymmetrischen Weg des durch die verschiedenen Filterstufen in den Spektrographen gelangenden Lichtbündels zuschreiben, weil wir auf den mit einer der vollen Filterhöhe entsprechenden, etwa 1 cm hohen Spaltenhöhe bereiteten Aufnahmen längs der Spektrallinien keine wesentliche Schwärzungsänderungen bzw. Schwärzungsfluktuationen beobachteten.

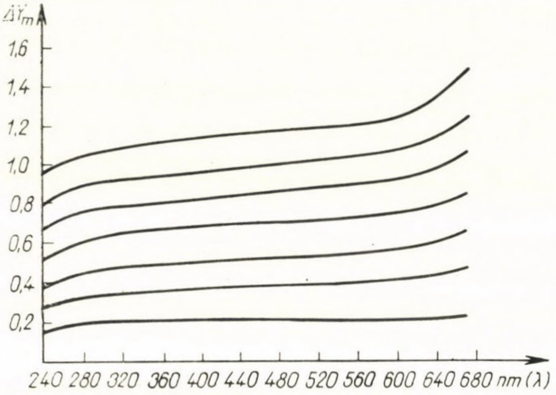

Abb. 6. Abhängigkeit der kalibrierten Filterkonstantenwerte des Neunstufenfilters des Spektrographen *ISP 28* von der Wellenlänge

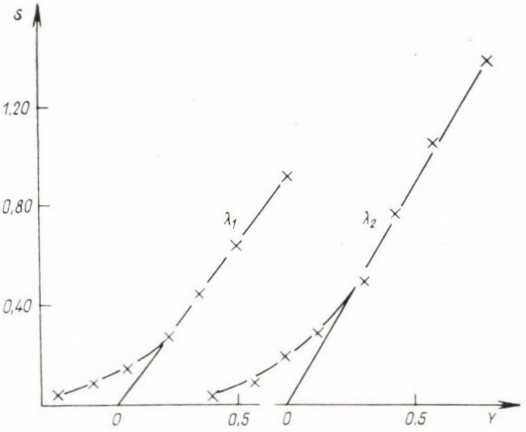

Abb. 7. Mittels Neunstufenfiltermethode aufgestellte Schwärzungskurven

$\lambda_1 = 319{,}71$ nm, $\gamma_1 = 1{,}31$ (bei Zweistufenfilter 1,23), $S_L = 0{,}30$, $S_E = 0{,}14$, $S_{0,10} = 0{,}09$
$\lambda_2 = 346{,}95$ nm, $\gamma_2 = 1{,}74$ (bei Zweistufenfilter 1,54), $S_L = 0{,}48$, $S_E = 0{,}19$, $S_{0,10} = 0{,}15$

Tabelle XXVI

Bei gleichen Wellenlängen gemessene γ-Werte im Falle von neunstufigen (9) bzw. zweistufigen (2) Filtern

λ (nm)	γ_9	γ_2
298,41	1,21	1,23
319,71	1,31	1,23
332,23	1,54	1,33
346,95	1,74	1,57
354,82	1,91	1,76

ZUSAMMENFASSUNG

Es werden die Ergebnisse verglichen, die bei der Untersuchung einiger, zur Aufstellung der Schwärzungskurve photographischer Platten dienenden Methoden erhalten wurden, sowie die charakteristischen Werte behandelt, die die Schwärzungskurve bzw. die reduzierte Schwärzungskurve kennzeichnen.

Es wird eine Methode zur Bestimmung der Steilheit der Schwärzungskurve mitgeteilt, die in solchen Fällen zu verwenden ist, in welchen an den Spektralaufnahmen nur so geringe Schwärzungen vorkommen, die dem unterexponierten Teil der Schwärzungskurve entsprechen.

Die Steilheit der Schwärzungskurve wurde im Falle von Emulsionen — Spektralplatten und Filmen — verschiedenen Typs, teilweise auch von sensibilisierten Emulsionen für den sichtbaren Spektralbereich bei verschiedenen Wellenlängen bestimmt. Nach Darlegung der Schwierigkeiten der Steilheitsbestimmung im sichtbaren Wellenlängenbereich wird die Lösung dieses Problems durch Verwendung eines Stufenfilters mit veränderlicher Filterkonstante besprochen.

Es wurde die Verwendbarkeit von Stufenfiltern verschiedener Typen geprüft, weiters die Abhängigkeit der Steilheit von der Spektrallinie, der Zeit und der Temperatur der Entwicklung sowie der Zusammensetzung des Entwicklers.

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ON THE KINETIC EQUATION OF UNIMOLECULAR HETEROGENEOUS CATALYTIC DECOMPOSITION PROCESSES

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In previous papers one of the authors and others [1, 2] have published a general kinetic equation of unimolecular heterogeneous catalytic decomposition processes, the differential form of which is:

$$w = \frac{kb_1 p_1}{\left(1 + \frac{k}{k_1'}\right)\left(1 + \sum_2^j b_i p_i\right) + \left(1 + \sum_2^j n_i \frac{k}{k_i'}\right) b_1 p_1} \tag{1}$$

where the symbols denote

w : rate of the process;
k, k_1', k_i' : rate constants of the surface chemical reaction, of the desorption of the initial component and the products and additional components, respectively;
b_1, b_i : adsorption coefficients of the initial component, products and additional components, respectively;
p_1, p_i : partial pressures of the initial component, the products and additional components, respectively;
j : number of all substances present;
n_i : stoichiometric coefficient of the i-th substance.

The equation was found to hold good for the dehydrogenation reaction of cyclohexane over ten nickel catalysts prepared in different ways [3] and over platinum [4], in the differential form; furthermore in the case of isopropyl alcohol dehydrogenation, in the integrated form [5].

In the derivation of Eq. (1), no assumption was made as to the rate-determining part played by one or more of the individual steps. On the other hand it was assumed that the surface states were stationary and the rates of individual steps could be described by LANGMUIR-type kinetics [6]. The equation is applicable, in principle, irrespective of the number of products and non-reacting additional components, and is of a general nature in this restricted sense only. Its applicability is limited, however, in two important respects. The derivation involves the assumption that the surface reaction consists of a single step. Furthermore, the equation is not valid in the case of the simultaneous decomposition of more than one component or, strictly speaking, in the case of parallel reactions. In the present paper the equation is extended to become applicable to these cases, too.

1. Unimolecular decomposition proceeding in two steps

Let us assume that substance A is transformed in two steps, by way of an intermediate B, into C in such a way that one or more molecules of the product X are eliminated in each step while stationary state adsorption prevails also for B. (Only in this case is the kinetic equation influenced by the presence of the intermediate product.) Let us assume further, as before, that the reaction takes place at a temperature and under a pressure where the rate of the backward reaction is practically negligible. In this case, the steps of the reaction will be the following:

$$
\begin{aligned}
&A + K \underset{v_1'}{\overset{v_1}{\rightleftarrows}} A \cdot K \\
&A \cdot K \xrightarrow{v_a} B \cdot K + n_a (X \cdot K) \\
&B \cdot K \underset{v_2}{\overset{v_2'}{\rightleftarrows}} B + K \\
&B \cdot K \xrightarrow{v_b} C \cdot K + n_b (X \cdot K) \\
&C \cdot K \underset{v_3}{\overset{v_3'}{\rightleftarrows}} C + K \\
&X \cdot K \underset{v_4}{\overset{v_4'}{\rightleftarrows}} X + K\,.
\end{aligned}
\tag{2}
$$

K denotes here the catalyst surface without referring to an active site of a definite structure or consisting of a definite number of atoms, so that the symbols $A \cdot K$ *etc.* simply refer to the adsorbed state.

The rates of the different steps figuring in the above scheme can be expressed by LANGMUIR kinetics as follows:

$$
\begin{aligned}
V_1 &= k_1 p_1 \; (1 - \Sigma\sigma) & V_1' &= k_1' \sigma_1 \\
V_a &= k_a \sigma_1 & V_b &= k_b \sigma_2 \\
V_2 &= k_2 p_2 \; (1 - \Sigma\sigma) & V_2' &= k_2' \sigma_2 \\
V_3 &= k_3 p_3 \; (1 - \Sigma\sigma) & V_3' &= k_3' \sigma_3 \\
V_4 &= k_4 p_4 \; (1 - \Sigma\sigma) & V_4' &= k_4' \sigma_4
\end{aligned}
\tag{3}
$$

where k_i : rate constants of the individual steps;
p_i : partial pressure of the components;
σ_i : coverage of the catalyst surface by component i.
(The indices 1, 2, 3 and 4 refer to substances A, B, C and X, respectively.)

By applying the principle of stationary states, the following equations may be set up:

$$V_1 - V_1' = V_a \tag{4,1}$$

$$V_2 - V_2' = V_b - V_a \tag{4,2}$$

$$V_3 - V_3' = - V_b \tag{4,3}$$

$$V_4 - V_4' = - (n_a V_a + n_b V_b) \tag{4,4}$$

$$V_a = V_b \tag{4,5}$$

By substituting the expressions from (3), and introducing the adsorption coefficients

$$b_i = \frac{k_i}{k_i'}$$

from Equations (4) we get:

$$b_1 p_1 (1 - \Sigma\sigma) - \sigma_1 = \frac{k_a}{k_1'} \sigma_1 \tag{5,1}$$

$$b_2 p_2 (1 - \Sigma\sigma) - \sigma_2 = \frac{1}{k_2'} (k_b \sigma_2 - k_a \sigma_1) \tag{5,2}$$

$$b_3 p_3 (1 - \Sigma\sigma) - \sigma_3 = - \frac{k_b}{k_3'} \sigma_2 \tag{5,3}$$

$$b_4 p_4 (1 - \Sigma\sigma) - \sigma_4 = - \left(n_a \frac{k_a}{k_4'} \sigma_1 + n_b \frac{k_b}{k_4'} \sigma_2 \right. \tag{5,4}$$

$$k_a \sigma_1 = k_b \sigma_2 \, . \tag{5,5}$$

Expressing σ_1 from the system of equations (5), we have:

$$\sigma_1 = \frac{b_1 p_1}{\left(1 + \frac{k_a}{k_1'}\right)(1 + b_3 p_3 + b_4 p_4) + \left[1 + \frac{k_a}{k_b} + \frac{k_a}{k_3'} + (n_a + n_b)\frac{k_a}{k_4'}\right] b_1 p_1} \tag{6}$$

Since in the stationary state, the rate of the overall process equals that of any individual step, we may write:

$$w = k_a \sigma_1 = \\ = \frac{k_a b_1 p_1}{\left(1 + \frac{k_a}{k_1'}\right)(1 + b_3 p_3 + b_4 p_4) + \left[1 + \frac{k_a}{k_b} + \frac{k_a}{k_3'} + (n_a + n_b)\frac{k_a}{k_4'}\right] b_1 p_1} \tag{7}$$

In the general case, taking into consideration that $n_a + n_b$ is the stoichiometric coefficient of X, eliminated in the process:

$$w = \frac{k_a b_1 p_1}{\left(1 + \frac{k_a}{k_1'}\right)\left(1 + \sum_{3}^{j} b_i p_i\right) + \left(1 + \frac{k_a}{k_b} + \sum_{3}^{j} n_i \frac{k_a}{k_i'}\right) b_1 p_1} \tag{8}$$

On comparing Eqs. (1) and (8), it is evident that the kinetic equation describing the rate of the process is only slightly influenced by making allowance for the formation of an intermediate dependence on the partial pressures of the components retains the same character, a difference showing up only in the coefficient of one of the members of the denominator, and instead of an overall k we have the rate constant of the first reaction step. It is clear, therefore, why Eq. (1) had correctly described the kinetics of cyclohexane dehydrogenation, although the reaction involves the intermediary formation of cyclohexene, as proved by labelling technique [7]. Moreover, the use of Eq. (1) is fully justified in this case, as the dehydrogenation of cyclohexene is much faster than that of cyclohexane [8], consequently the term k_a/k_b is negligible.

2. Kinetic equation of unimolecular heterogeneous catalytic reaction: Simultaneous reaction of two substances when one of the products is common

On simultaneously feeding A and C, B and D are formed with the elimination of X. Assuming a single step surface reaction, the reaction scheme for the two substances will be:

$$\begin{array}{ll}
A + K \underset{V_1'}{\overset{V_1}{\rightleftharpoons}} A \cdot K & C + K \underset{V_4'}{\overset{V_4}{\rightleftharpoons}} C \cdot K \\
A \cdot K \xrightarrow{V_a} B \cdot K + n_x X \cdot K & C \cdot K \xrightarrow{V_c} D \cdot K + n_x X \cdot K \\
B \cdot K \underset{V_2}{\overset{V_2'}{\rightleftharpoons}} B + K & D \cdot K \underset{V_5}{\overset{V_5'}{\rightleftharpoons}} D + K \\
\multicolumn{2}{c}{X \cdot K \underset{V_3}{\overset{V_3'}{\rightleftharpoons}} X + K}
\end{array} \tag{9}$$

(In accordance with the example chosen — simultaneous dehydrogenation of cyclohexane and methylcyclohexane — n_x was assumed to be equal for both reactions.)

Denoting the values of surface coverage for the substances A, B, X, C and D, in the order presented, by σ_1, σ_2, σ_3, σ_4 and σ_5, and the partial pressures by the corresponding p_i symbols, expressing of the individual rates by Langmuir's kinetic law for surface adsorption [6] leads to the following system of equations:

$$V_1 - V_1' = V_2' - V_2 = V_a = k_a \sigma_1; \quad V_4 - V_4' = V_5' - V_5 = k_c \sigma_4;$$
$$V_3' - V_3 = n_x (k_a \sigma_1 + k_c \sigma_4) \tag{10}$$

$$k_1 p_1 (1 - \Sigma\sigma) - k_1' \sigma_1 = k_a \sigma_1 \qquad k_4 p_4 (1 - \Sigma\sigma) - k_4' \sigma_4 = k_c \sigma_4$$
$$k_2 p_2 (1 - \Sigma\sigma) - k_2' \sigma_2 = - k_a \sigma_1 \qquad k_5 p_5 (1 - \Sigma\sigma) - k_5 \sigma_5 = - k_c \sigma_4$$
$$k_3 p_3 (1 - \Sigma\sigma) - k_3' \sigma_3 = - n_x (k_a \sigma_1 + k_c \sigma_4) \, . \tag{11}$$

After solving the system for σ_1 and taking into consideration relation $w_a = k_a \sigma_1$, the expression for the stationary rate of decomposition of substance A will be:

$$w_a = \frac{k_a b_1 p_1}{\left(1 + \frac{k_a}{k_1'}\right)(1 + b_2 p_2 + b_3 p_3 + Q_c b_4 p_4 + b_5 p_5) + \left(1 + \frac{k_a}{k_2'} + n_x \frac{k_a}{k_3'}\right) b_1 p_1} \tag{12}$$

where

$$Q_c = \frac{1 + n_x \frac{k_c}{k_3'} + \frac{k_c}{k_5'}}{1 + \frac{k_c}{k_4'}}$$

Evidently, the expression for w_b, the rate of decomposition of the other component, will be completely analogous.

As it may be seen, Eq. (11) is analogous to the expression obtained from the general Eq. (1) for the case of one nonreacting additional component. The presence of coefficient Q_c accounts for the fact that substance C takes also part in the reaction. Q_c is frequently substantially simplified by singling out the rate controlling step. Thus, *e.g.*, if

$$k_c \ll k_3', k_4', k_5'$$

i.e., the surface reaction is rate determining in the overall process, one can set

$$Q_c = 1 \, .$$

The reaction of the additional component has therefore, in this case, no influence on the LANGMUIR—HINSHELWOOD kinetic equations; only the presence of the reaction product has to be taken into consideration.

Let us now examine the application of the equation to an actual reaction, the dehydrogenation of a mixture of methyl-cyclohexane and cyclohexane. Experimental results are at our disposal from an earlier paper [9] in which, however, calculations were based on the assumption that methyl-cyclohexane, like hydrogen or benzene, would act only as a diluent, while Eq. (12) takes into account that the dehydrogenation of methyl-cyclohexane and cyclohexane are parallel processes.

By substituting the partial pressures in Eq. (12) by values from the formula

$$p_i = N_i P$$

(N_i being the mole fraction of the given substance and P the total pressure), and bearing in mind the previously proved fact that the flow velocities of the components (v_1 and v_4) exceed by far the rate of formation of the product (x), in a flow system and at atmospheric pressure, the following relation holds between the rate of cyclohexane dehydrogenation and the methylcyclohexane to cylohexane ratio:

$$\frac{1}{w_{\mathrm{CH}}} = \frac{1}{k_{\mathrm{CH}}\, b_1}\left[1 + \frac{k_{\mathrm{CH}}}{k_1'} + \left(1 + \frac{k_{\mathrm{CH}}}{k_2'} + 3\,\frac{k_{\mathrm{CH}}}{k_3'}\right) b_1\right] + \\ + \frac{1 + \dfrac{k_{\mathrm{CH}}}{k_1'}}{k_{\mathrm{CH}}\, b_1}\,(1 + Q_{\mathrm{MCH}} \cdot b_4)\,\frac{v_4}{v_1} \tag{13}$$

$$Q_{\mathrm{MCH}} = \frac{1 + \dfrac{3k_{\mathrm{MCH}}}{k_3'} + \dfrac{k_{\mathrm{MCH}}}{k_5'}}{1 + \dfrac{k_{\mathrm{MCH}}}{k_4'}} \tag{14}$$

Let us accept the values $Q_{\mathrm{MCH}} b_4$ as the apparent adsorption coefficients of methylcyclohexane since they are proportional to, and in the limiting case identical with, the adsorption coefficients of methylcyclohexane, and denote them by $\bar{b}_4$.

For the dehydrogenation of cyclohexane in mixtures of cyclohexane and argon, taking into consideration that the adsorption coefficient of argon is zero, it follows from Eq. (1) that:

$$\frac{1}{w_{\mathrm{CH}}}=\frac{1}{k_{\mathrm{CH}}\,b_1}\left[1+\frac{k_{\mathrm{CH}}}{k_1'}+\left(1+\frac{k_{\mathrm{CH}}}{k_2'}+3\,\frac{k_{\mathrm{CH}}}{k_3'}\right)b_1\right]+$$

$$+\frac{1+\dfrac{k_{\mathrm{CH}}}{k_1'}}{k_{\mathrm{CH}}\,b_1}\cdot\frac{v_6}{v_1} \tag{15}$$

where v_6 is the flow velocity of argon.

Equations (13) and (15) both define a linear relationship between $1/w_{\mathrm{CH}}$ and v_4/v_1 and v_6/v_1, respectively.

$$\frac{1}{w_{\mathrm{CH}}}=\alpha_{\mathrm{CH}}+\gamma_4\cdot\frac{v_4}{v_1} \tag{13a}$$

$$\frac{1}{w_{\mathrm{CH}}}=\alpha_{\mathrm{CH}}+\gamma_6\cdot\frac{v_6}{v_1} \tag{15a}$$

The value of $\bar{b}_4$ may be calculated from the slopes of the straight lines defined by (13a) and (15a):

$$\bar{b}_4=\frac{\gamma_4}{\gamma_6}-1 \tag{16}$$

The experimental results, obtained in the case of the dehydrogenation of mixtures of methylcyclohexane and cyclohexane have confirmed relations (13a) and (15a) [9]. Values for different temperatures are quoted in Table I.

The correctness and applicability of the equations thus derived can easily be verified. The apparent adsorption coefficient of cyclohexane may be calculated from Eq. (15). Using the notation introduced in Eq. (15a):

$$\frac{\alpha_{\mathrm{CH}}-\gamma_6}{\gamma_6}=\frac{1+\dfrac{k_{\mathrm{CH}}}{k_2'}+3\,\dfrac{k_{\mathrm{CH}}}{k_3'}}{1+\dfrac{k_{\mathrm{CH}}}{k_1'}}\,b_1=Q_{\mathrm{CH}}\cdot b_1=\bar{b}_1 \tag{17}$$

In a previous paper (2) the values of a_{CH} and γ_6 had been determined from measurements of dehydrogenation of mixtures of cyclohexane and argon on the given catalyst but the values of $\bar{b}_1$, analogous to $\bar{b}_4$, were not calculated. These are now listed in Table II.*

---

*The values of α_{CH} and γ_6 slightly differ from those given formerly [2] since graphic evaluation has been replaced by a more precise numerical method.

Comparison of the data of Tables I and II reveal a resemblance of the numerical values of the apparent adsorption coefficients of the two substances, which is rather close in view of the difference of their molecular weights.

Table I

Kinetic data of the dehydrogenation of methylcyclohexane—cyclohexane mixtures.
Catalyst: nickel. Rate of cyclohexane feed: 13 ml NTP/min

t, °C	α_{CH}	γ_4	γ_6*	$\bar{b}_4$, atm^{-1}
271	1.03	1.579	0.406	2.88
290	0.73	0.832	0.204	3.08
299	0.37	0.800	0.158	4.06
309	0.37	0.570	0.115	3.95
317	0.34	0.511	0.087	4.78

* Interpolated to the given temperature from directly measured data of Table II.

Table II

Kinetic data of the dehydrogenation of cyclohexane—argon mixtures.
Catalyst: nickel. Rate of cyclohexane feed: 12 ml NTP/min

t, °C	α_{CH}	γ_6	$\bar{b}_1$, atm^{-1}
278	0.85	0.309	1.78
293	0.64	0.200	2.20
310	0.48	0.111	3.32
320	0.39	0.087	3.48

By inter- (extra) polating the values of $\bar{b}_1$ and $\bar{b}_4$ to identical temperatures, we find:

	275 °C	300 °C	325 °C
$\bar{b}_1$ (atm^{-1})	1.95	2.70	3.68
$\bar{b}_4$ (atm^{-1})	2.85	3.80	5.95

The resemblance of the data is still more striking if the values of $\lg \bar{b}_i$ are plotted against $1/T$ (Fig. 1) and the apparent adsorption enthalpies are calculated from the slopes of the straight lines, 8 kcal/mole being obtained in both

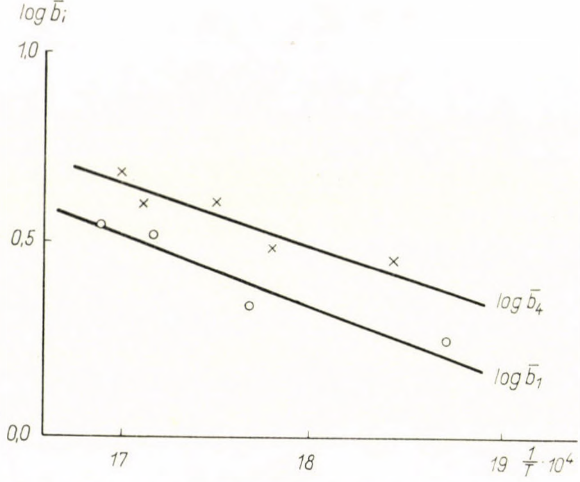

Fig. 1. Straight lines obtained by transformation of the data of temperature dependence of the apparent adsorption coefficients of methylcyclohexane and cyclohexane

cases. This fact, besides confirming the equations used, indicates the identity of the kinetic parameters characterizing the dehydrogenation of the two substances.

3. Adsorption coefficients and kinetics of the dehydrogenation of cyclohexane

The values of the apparent adsorption coefficients of cyclohexane may be calculated for various nickel catalysts prepared in different ways [3] as well as for platinum [4] and rhodium catalysts. These values are listed in Table III. As it may be seen, they are of the same order of magnitude, and their temperature dependence is of the same character as has been found with the previous nickel catalyst (Ni No. 1).

The expression for the apparent adsorption coefficient is remarkably simplified if attention is paid to the lately established fact [10, 11] that cyclohexene and cyclohexadiene are dehydrogenated with a rate exceeding that of cyclohexane by one and two orders of magnitude, respectively. From this fact it follows, in contrast with former views of one of the authors based on indirect evidence [12], that the desorption of benzene and hydrogen is much faster than the other steps of the dehydrogenation process of cyclohexane.

Therefore*

$$k_{\mathrm{CH}}, k_1 \ll k_2', k_3' . \tag{18}$$

---

*In earlier papers [3, 12] it has been shown that the adsorption of cyclohexane cannot be the only rate controlling step.

Table III

Apparent adsorption coefficients of cyclohexane on various metal catalysts

Catalyst*	t, °C	b_1, atm^{-1}	Catalyst*	t, °C	$\bar{b}_1$ atm^{-1}
Ni No. 4	250	1.54	Ni No. 9	270	0.51
	258	1.14		280	0.48
	261	1.69		290	1.03
	270	2.40		300	0.94
	280	3.00		310	1.01
	282	4.23	Pt	280	7.7
	289	4.26		290	11.7
	299	4.87		305	14.0
Ni No. 5	261	1.32		316	32.3
	284	2.69	Rh	250	1.13
	300	3.34		260	1.65
	309	3.65		270	2.38
	320	5.40		280	5.22
Ni No. 8	280	0.61		290	4.50
	290	0.76		300	5.34
	300	1.42			
	300	1.44			
	310	2.60			

* Numbering of the Ni catalysts refers to different modes of preparation see [3].

Taking into consideration inequality (18), the expression of the apparent adsorption coefficient modifies to

$$\bar{b}_1 = \frac{b_1}{1 + \dfrac{k_{\mathrm{CH}}}{k_1'}} \tag{19}$$

or, because of $b_1 = k_1/k_1'$,

$$\bar{b}_1 = \frac{k_1}{k_1' + k_{\mathrm{CH}}} \tag{19a}$$

Evidently, the value of $\bar{b}_1$ can rightfully be called the apparent adsorption coefficient of cyclohexene, since the rate constant of formation of the adsorbed cyclohexane is in the numerator while the denominator contains the sum of the rate constants of the two opposed processes, namely desorption and surface reaction leading to decomposition.

From results of independent, but similar kinetic experiments, the true adsorption coefficient of cyclohexane on nickel [13] can be estimated. As this is of the order of 10^2, it is justly assumed that

$$k_1 \gg k_1' \,. \tag{20}$$

From the values of $\bar{b}_1$ figuring in Tables II and III, however, it follows that k_1 and k_{CH} are of the same order of magnitude. Consequently, the apparent adsorption coefficient is the ratio of the rate constants of adsorption and surface reaction, and the rate of dehydrogenation is controlled by both the adsorption and surface reaction of cyclohexane.

Plotting the logarithms of the $\bar{b}_1$ values against $1/T$, the apparent heat of adsorption, $\Delta \bar{H}_1$, may be calculated from the slopes of the resulting straight lines by the following equation:

$$\bar{b}_1 = \bar{b}_1^0 \exp\left(\frac{\Delta \bar{H}_1}{RT}\right) \tag{21}$$

where

$$\Delta \bar{H}_1 = \varepsilon_1 - \varepsilon_{\mathrm{CH}} \,.$$

Thus the value of the apparent heat of adsorption is the difference between the energies of activation of the two rate controlling processes.

Values of $\Delta \bar{H}_1$ found for the different metal catalysts are collected in Table IV.* These are found to be positive for every catalyst, the activation energy

Table IV

Apparent enthalpies of adsorption as calculated from the constants of the kinetic equation, and activation energies of adsorption and surface reaction (kcal/mole)

Catalyst	$\Delta \bar{H}_1$	ε_1	ε_{CH}
Ni No. 1	13	23	10
4	19	29	10
5	13	18	5
8	10	22	11
9	15	20	5
Pt	15	28	13
Rh	18	28	10

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*On basis of the analogy of the kinetic relations for the different metals, inequality (20) is assumed to be valid for all metals, although it was verified experimentally for nickel catalyst No. 1 only.

for cyclohexane adsorption, therefore, being greater than that of the surface reaction.

The numerical values of the energy of activation of cyclohexane adsorption can also be determined from the temperature dependence of the slope of the straight line given by Eq. (15) describing the dehydrogenation of cyclohexane in the presence of argon. As it is, the values

$$\gamma_6 = \frac{1 + \dfrac{k_{\mathrm{CH}}}{k_1'}}{k_{\mathrm{CH}}\, b_1}$$

are, if inequality (20) and the orders of magnitude of the $\bar{b}_1$ values are taken into consideration, the reciprocals of the cyclohexane adsorption rate constants. The values of ε_1 calculated from the temperature dependence — taken from a previous paper [4] — are also listed in Table IV, together with the activation energies of surface reaction calculated from Eq. (21).

It may be seen from Table IV that both the adsorption of cyclohexane and the surface reaction are processes requiring considerable activation. Since the surface reaction involves, as it is, the rupture of a C—H bond, adsorption requiring an energy of activation in excess by 10—20 kcal/mole must of necessity be a dissociative process, too. This statement supports the former assumption concerning the dissociative adsorption of cyclohexane [3], based on evidence from literature. The activation energy of cyclohexane adsorption, largely surpassing that of the surface reaction, also agrees with the experimental fact mentioned earlier that the rate of dehydrogenation of rings containing π-bonds is much higher than that of saturated hydrocarbon rings. The fact that unsaturated hydrocarbons are more easily adsorbed than saturated ones is well known.

The numerical values of the apparent adsorption coefficients and the energies calculated from their temperature dependence, together with the recent experimental evidence, thus corroborate the earlier statements of one of the authors [12] about the mechanism and the kinetics of cyclohexane dehydrogenation. Summing up, it may be stated that the rate of the process is controlled by the rates of both the dissociative adsorption of cyclohexane and the surface reaction. The activation energy required by these steps is larger for cyclohexane adsorption, therefore $\Delta\bar{H}_1$ (and, of course, $\Delta\bar{H}_4$ for methylcyclohexane) is positive. As the inverse of dissociative adsorption, desorption does not affect the picture under the given conditions, the true enthalpy of adsorption cannot be inferred from kinetic measurements. Thus correctness of the assumption of an endothermic adsorption [9] remains still undecided.

SUMMARY

The possibility has been examined to extend the scope of the kinetic equation for unimolecular heterogeneous catalytic reactions, derived and verified earlier, to the case of a surface reaction proceeding in two steps and for a mixture containing two reacting components. The equations thus obtained are similar in form to those derived for the simpler case. The correctness of the equation is supported by experimental results obtained in the simultaneous dehydrogenation of methylcyclohexane and cyclohexane. The results unequivocally show that the first step in the dehydrogenation of cyclohexane and related compounds is dissociative adsorption followed by a surface reaction involving the final elimination of hydrogen. These two processes jointly control the rate.

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KINETICS AND MECHANISM OF SUBSTITUTION REACTIONS OF COMPLEXES, IV*

THERMAL DECOMPOSITION OF COMPLEXES OF THE TYPE $[Co(Cy)_2Amin_2]X$

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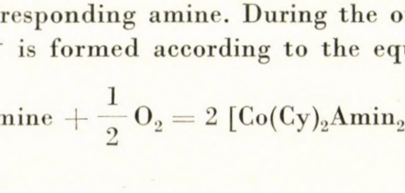
We synthetized a great number of new complexes of the type $[Co(Cy)_2Amin_2]X$, where Cy means 1,2-cyclohexanedionedioxime (nioxime). The amine (Amin) was aniline, *o*-, *m*- and *p*-toluidine, *o*- and *p*-ethylaniline, *o*- and *p*-anisidine, X was Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^- and complex anions as $[Co(NH_3)_2(NO_2)_4]^-$, $[Cr(NH_3)_2(SCN)_4]^-$, $[Cr(SCN)_6]^{3-}$.

These binary salts were obtained by oxidizing an alcoholic aqueous solution of Co(II) salt, by air bubbling, in the presence of 1,2-cyclohexanedione dioxime and of the corresponding amine. During the oxydation the complex cation $[Co(Cy)_2Amin_2]^+$ is formed according to the equation

$$2\,Co^{2+} + 4\,Cy_2 + 6\,\text{Amine} + \frac{1}{2}O_2 = 2\,[Co(Cy)_2Amin_2]^+ + 2\,\text{Amin}\cdot H^+ + H_2O\,.$$

From the solution obtained the salt was separated by means of a double exchange reaction.

Concerning the structure of these complexes, a similar one as in the case of the corresponding dimethylglyoxime complexes can be assumed. In the dimethylglyoxime complexes there is supposed a hydrogen bridge between the two molecules of oxime [1], which is possible only if these oxime molecules occupy the octahedron plane and the amine molecules (Amin) are in *trans* position. As our cyclohexanedione dioxime complexes were obtained under similar condition, we can suppose the following structure for the octahedron plane of the complex cation:



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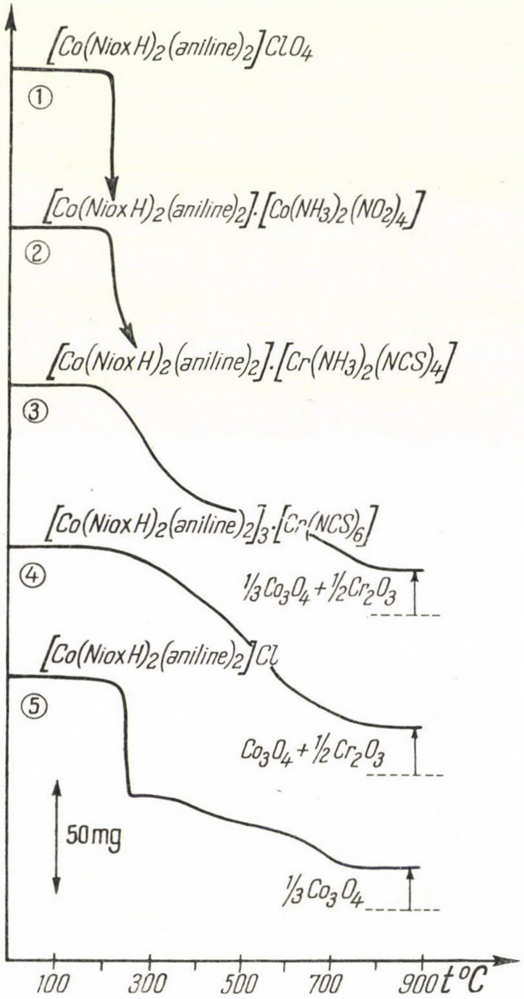


Fig. 1. The thermograms of some [Co(Cy)$_2$Aniline$_2$]X salts

We studied the behaviour of these complexes by thermogravimetric analysis. As in the case of the dimethylglyoxime complexes, we could observe three types of thermograms. The salts of oxidizing anions (ClO_4^-, NO_3^-, $[Co(NH_3)_2(NO_2)_4]^-$) decompose quickly, explosively, between 180 and 250°. The salts of thiocyanate containing complex anions $[Cr(NH_3)_2(SCN)_4]^-$, $[Cr(SCN)_6]^{3-}$ show a slow pyrolysis, without the formation of well defined intermediates (Fig. 1). In the case of thiocyanates, iodides, bromides and sometimes also chlorides, one can observe on the thermograms a weight loss stop, corresponding to the loss of one molecule of aromatic amine. This weight loss stop is more definite in the case of thiocyanates and iodides, and less definite with chlorides

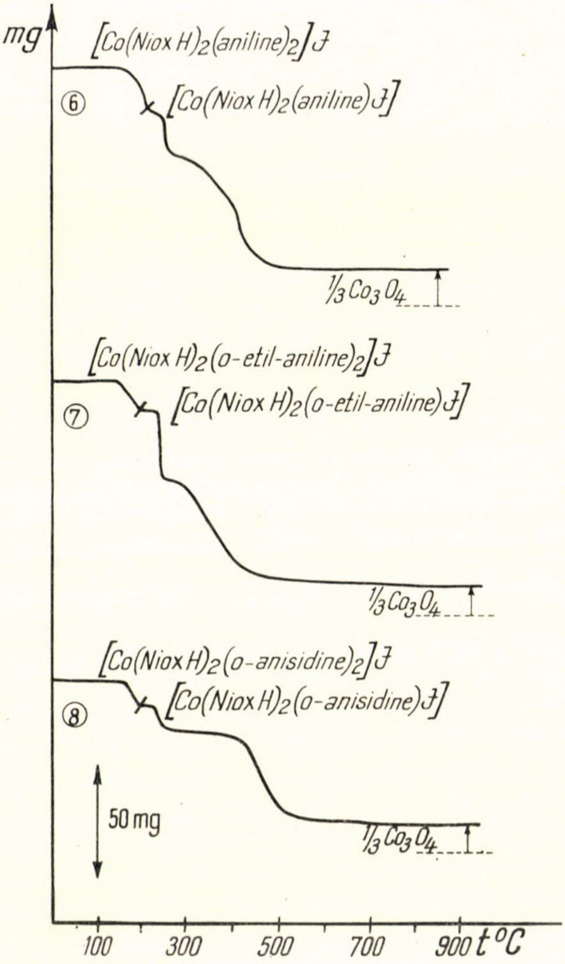


Fig. 2. The thermograms of some [Co(Cy)$_2$Amin$_2$]I complexes

(Figs. 1—2). The behaviour of these complexes is thus perfectly analogous to the behaviour of the corresponding dimethylglyoxime complexes [2].

On the analogy with dimethylglyoxime complexes, where we have shown, that the first stage of the thermal decomposition is a substitution reaction [3], we can suppose that the first weight loss stop corresponds to the formation of a stable nonelectrolytic intermediate, according to the equation

$$[\mathrm{Co(Cy)_2Amin_2}]^+ + \mathrm{X}^- = [\mathrm{Co(Cy)_2Amin\,X}] + \mathrm{Amin}$$

As the reaction leads to the formation of a single solid intermediate and of a gaseous product, the kinetics of the process can be studied by means of

HOROWITZ and METZGER's method [4]. In the case of first order reactions these authors found the following equation to be valid

$$\ln \ln \frac{W_0 - W_t}{W - W_t} = \ln \ln \frac{1}{x} = \frac{E^*}{RT_s^2} \vartheta \tag{1}$$

where W_0, W_t and W are the initial, the final and the actual weight of the sample, respectively, E^* is the activation energy, R = the gas constant, T_s = the temperature in °K when the molar fraction x of the initial complex is equal to $\frac{1}{e}$ and ϑ is the relative temperature, according to the equation $\vartheta = T - T_s$. A plot of $\lg \lg \frac{1}{x}$ *versus* ϑ gives a straight line with the slope $E^*/2.3\,RT_s^2$, which allows the calculation of E^*.

In the case of second order reactions we have

$$\ln \left(\frac{1}{x} - 1 \right) = \frac{E^*}{RT_s^2} \vartheta \tag{2}$$

and a plot of $\lg \left(\frac{1}{x} - 1 \right)$ versus ϑ gives also a straight line with the same slope as before.

From the obtained T_s and E^* data it is possible to calculate the frequency factor Z of Arrhenius' equation with the formula [5]:

$$Z = q \frac{E^*}{RT_s^2} \exp \left\{ \frac{E^*}{RT_s} \right\} \tag{3}$$

where q is the rate of heating: $q = \frac{dT}{dt}$.

The activation entropy ΔS^* can be obtained from Z using the known correlation

$$\Delta S^* = 2.3\,R \lg \frac{Zh}{kT} \tag{4}$$

where h is the Planck constant, k = the Boltzmann constant.

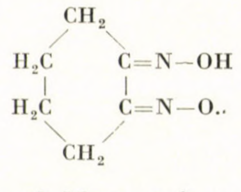
During pyrolysis, a relatively stable intermediate was formed by the majority of studied compounds, which at higher temperature decomposes, too. On the thermogravimetric curves (Fig. 2) the theoretical position of the non-electrolytic intermediate $[Co(Cy)_2Amin\ X]$ is marked. The final product of the pyrolysis was Co_3O_4 in all the cases (see also Table I).

Table I

Stoichiometric data for the thermal decomposition of complexes of the type $[Co(Cy)_2\ (Am)_2]X$

X	Am	Weight of the sample mg	Nonelectrolyte		T, °C	mg Co_3O_4 (920 °C)	
			Calcd. mg	Found mg		Calcd.	Found
Cl	aniline	100.6	83.4	—	—	14.3	13.8
Br	aniline	101.8	86.2	96	240	13.4	12.9
I	aniline	104.2	89.2	88.8	210	12.77	12.8
NCS	aniline	100.8	84.1	84.7	220	13.9	14.0
Br	*o*-toluidine	100.5	83.5	83	162	12.6	12.0
I	*o*-toluidine	100.5	84.7	—		11.8	11.3
NCS	*o*-toluidine	100.3	82.8	90	210	13.1	12.0
Cl	*m*-toluidine	100.6	82.2	97	240	13.66	13.6
Br	*m*-toluidine	101.0	83.9	—	—	12.75	12.4
I	*m*-toluidine	100.8	84.9	88	220	11.8	11.3
NCS	*m*-toluidine	100.1	82.6	83.5	210	13.2	13.6
Cl	*p*-toluidine	100.4	82.2	—	—	13.6	13.6
Br	*p*-toluidine	100.4	83.5	83	—	12.68	12.58
I	*p*-toluidine	100.2	84.6	84.4	210	11.7	11.0
NCS	*p*-toluidine	101.0	83.5	84.1	204	13.2	12.9
$Br \cdot H_2O$	*o*-ethyl-aniline	100.7	80.6	82	220	11.9	12.2
I	*o*-ethyl-aniline	100.9	83.6	85	216	11.4	10.8
Cl	*p*-ethyl-aniline	100.2	80.5	—	—	12.9	12.0
Br	*p*-ethyl-aniline	100.7	82.3	95	230	12.18	12.1
I	*p*-ethyl-aniline	101.1	84	88	200	11.4	11.5
NCS	*p*-ethyl-aniline	50.0	40.5	40	196	6.3	6.9
Cl	*o*-anisidine	100.6	80.7	80.3	176	12.9	12.0
I	*o*-anisidine	100.1	82.8	81	216	11.2	—
NCS	*o*-anisidine	100.3	81	82	200	12.5	12.8
$Cl \cdot 2H_2O$	*p*-anisidine	100.3	80.5	90	232	12.9	12.8
Br	*p*-anisidine	102.0	83.3	—	—	11.7	11.4
I	*p*-anisidine	101.3	83.8	90	200	11.4	11.9
$NCS \cdot H_2O$	*p*-anisidine	100.8	79.5	81	220	12.17	12.1

“Cy” =



We applied HOROWITZ and METZGER’s method to the 28 chlorides, bromides, iodides and thiocyanates and we could approximately linearize the thermogravimetric curves in the case of 19 complexes with equation (1) or (2), in the majority of the cases with both. In 9 cases it was impossible to obtain a straight line, especially with chlorides. From the straight lines obtained we calculated the activation energies E^* and the decomposition temperatures T_s. By means of the equations (3) and (4) we obtained the entropies of the activation ΔS^*. The obtained data, together with the explosion temperatures of the perchlorates, are given in Table II. In the first column the co-ordinated amine, in the others T_s, E^* and ΔS^* data are given.

Table II

Kinetic data for the substitution reaction $[Co(Cy)_2Amin_2]\ X = [Co(Cy)_2Amin\ X] + Amin$

Amine	Decomposition temperature T_s in °K					Activation energy E^*, kcal/mole				Activation entropy ΔS^*, e. u.			
	Cl	Br	I	SCN	ClO_4	Cl	Br	I	SCN	Cl	Br	I	SCN
aniline	—	527	490	461	500	—	26	28	38	—	−19	−13	+15
o-toluidine	—	441	—	—	496	—	37	—	—	—	+17	—	—
m-toluidine	—	—	473	465	507	—	—	33	47	—	—	+1	+33
p-toluidine	—	—	475	474	488	—	—	28	36	—	—	−9	+8
o-ethylaniline	—	458	441	—	485	—	24	31	—	—	−16	+3	—
p-ethylaniline	—	529	477	395	497	—	22	31	31	—	−28	−3	+12
o-anisidine	465	—	457	425	512	34	—	38	30	+4	—	+16	+3
p-anisidine	—	479	476	475	491	—	31	28	28	—	+3	−10	−9

The interpretation of these data is very difficult, because the studied process, being heterogeneous, is very complicated. Diffusion can play a very important role, and the activation energy can be influenced by the crystal lattice energy. In spite of these difficulties we tried to give an explanation in the case of the analogous dimethylglyoxime complexes, assuming that the reaction rate is determined by the rate of the substitution reaction [2].

Assuming that the chemical reaction is the rate determining process, on the basis of our experimental data we can suppose that the substitution reaction takes place according to an S_N2 mechanism, or a competition between S_N1 and S_N2 mechanisms is possible. Assuming an S_N2 mechanism, we can expect an increasing reaction rate, *i.e.* decreasing decomposition temperature, with increase of the nucleophylic force of the attacking agent X^-. The nucleophylic force of the anions considered increases in the sequence $Cl^- < Br^- < I^- < SCN^-$ according to the values of their electron donor constants [6]. As the thiocyanate ion can give a multiple bond with cobalt that is a more stable intermediate complex than I^-, the decrease of the decomposition temperature in the order $Cl^- > Br^- > I^- > SCN^-$ (having, of course, the same co-ordinated amine) can be expected. As seen from Table II, the expected rule is valid in all the studied cases sometimes however, the differences are not very significant.

If we assume an S_N2 mechanism, the activated complex must have the co-ordination number 7. The loss of C.F.S.E. (crystal field stabilization energy) in a bipyramidal intermediate, compared to the octahedral complex, is about 47 kcal/mole [7]. The presumed structure of our complexes makes the formation of a pentagonal bipyramidic intermediate hardly probable, because of the hydrogen bridges. We can suppose rather the formation of an intermediate, like that shown in Fig. 3. In this case the C.F.S.E. must be less than the value given above, but greater than about 20 kcal, which corresponds to the dissociation mechanism [7]. The mean value of the activation energy in our experiments was $32 + 2$ kcal for the 19 complexes studied in good agreement with the above considerations.

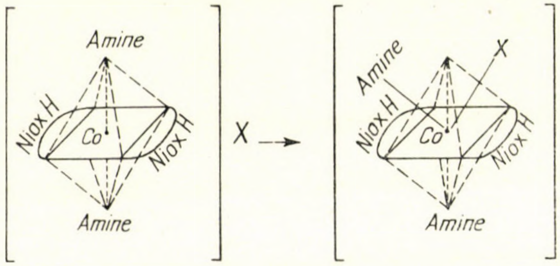


Fig. 3. The formation of the presumed activated intermediate

As seen from Table II, the average values apart from those for bromides, iodides and thiocyanates, do not differ essentially from this value, although one can observe a slight tendency of increase from bromides to thiocyanates. Comparing the mean values obtained with those found for the corresponding dimethylglyoxime complexes (Table III), we can see that they are a little

Table III

Comparison of the mean activation energies and entropies of 1,2-cyclohexanedione dioxime (Cy) complexes with analogous data for dimethylglyoxime (DH) complexes

		Cl	Br	I	SCN
Mean activation energy, Kcal/mole	Cy	—	28±2.7	31±1.4	35±2.9
	DH	36±4.1	32±2.8	36±2.4	37±3.3
Mean activation entropy, e. u.	Cy	—	−9±9.1	−2±3.8	+10±5.7
	DH	+4±10	−2±5.2	+12±5.4	+14±7.9

smaller in the case of 1,2-cyclohexanedione dioxime complexes. In the same time the decomposition temperatures are generally a little higher than in the case of the corresponding dimethylglyoxime complexes. Comparison of the bromides, iodides and thiocyanates of the same series, and comparison of dimethylglyoximes and cyclohexane-dione dioxime complexes show that decrease of decomposition temperatures is accompanied by a tendency of increase of the activation energy. This means that for the decreases of T_s the entropy factor is responsible. As seen from Tables II and III the entropy values obtained are very scattered and do not enable us to draw reliable conclusion. Nevertheless we can observe an increase of the activation entropy in the same direction in which the activation energy increases. The activation entropy appears to be positive in the case of thiocyanates in both series, but only with dimethylglyoxime complexes in the case of iodides, in the other compounds having near zero or negative values. Owing to the very scattered experimental values, this entropy effect is uncertain and also theoretically can be hardly interpreted.

We consider that our kinetic data are not reliable enough to support with certainty our hypotheses concerning the mechanism of the substitution. In order to arrive at reliable conclusions it is undoubtedly necessary to study this reaction under more controllable conditions.

Experimental part

The synthesis of the Co(III) nioximine complexes. To 5 g of Co(CH$_3$COO)$_2$ 4 H$_2$O (20 mmoles), dissolved in 100 ml water, is added 5.7 g 1,2-cyclohexanediondioxime (40 mM) and 60 mM of aromatic amine (aniline derivatives with pK $<$ 11) dissolved in 200 ml ethanol. The obtained brown solution is oxidized by a strong current of air bubbling for 5—7 hours. The solution is made up to 600 ml with 50% alcohol and filtered. The concentration of the obtained [Co(Cy)$_2$Amine$_2$] CH$_3$COO solution is approximately 33.3 mM/l.

From this acetate solution a great number of products can be obtained by the means of double exchange reactions. The anions of smaller ion radii as Cl$^-$, Br$^-$, SCN$^-$ precipitate generally the corresponding complex salts only from concentrated solutions after longer standing. The voluminous anions as ClO$_4^-$, I$^-$, picrate and complex anions as [Co(NH$_3$)$_2$(NO$_2$)$_4$]$^-$, [Cr(SCN)$_6$]$^{3-}$ precipitate nearly quantitatively the considered complex cations even from dilute solutions.

The solubility of the complex salts depends, besides the anion also on the nature of the co-ordinated amine molecules (*e.g.* the *p*-toluidine, *p*-ethylaniline and *p*-anisidine derivatives are a little more soluble than the corresponding ortho derivatives).

From the acetate solution the crystalline [Co(Cy)$_2$Amin$_2$]X salts were obtained as follows:

To 60 ml acetate solution (containing 2 mM) is added a volume of 20—100 ml NaX or HX solution. After standing for 4—12 hours the crystalline product is filtered of, washed with small quantities of water and dried on air. The utilized quantities of the reagents were:

20—100 ml of 10% NaCl solution
20— 30 ml of 30% HBr or NaBr solution
30 ml of 5% KI solution
50 ml of 10% HClO$_4$ solution
20— 50 ml of 25% NaCNS solution

o-toluidine and *o*-anisidine derivatives precipitate only after standing for 3—4 days.

Table IV

New complexes of type [Co(Cy)$_2$Am$_2$]X

No.	Am	X	Mol. weight	Analysis		Appearance	Yield %
				Calcd.	Found		
1.	aniline	Cl	562.9	Co 10.48 N 14.93	10.25 14.40	thin yellow-brown needles	65
2.	aniline	I	654.4	Co 9.00 N 12.85	9.01 12.75	thin brown acicular cryst.	85
3.	aniline	NCS	585.6	Co 10.07 N 16.75	10.10 16.74	yellow-brown short prisms	85
4.	*o*-toluidine	Br	635.4	Co 9.27 N 13.22	9.06 13.33	fibrous brown prisms	30
5.	*o*-toluidine	I	682.4	Co 8.62 N 12.31	8.26 12.25	brilliant brown hexagonal plates	75
6.	*o*-toluidine	NCS	613.6	Co 9.60 S 5.22	9.51 5.29	red-brown prisms	40
7.	*o*-toluidine	ClO$_4$	655	Co 8.99	9.03	brown irregular prisms	70
8.	*m*-toluidine	Cl	591	Co 9.97 N 14.22	9.93 14.31	thin brown rectangular plates	70
9.	*m*-toluidine	Br	635.4	Co 9.27 N 13.22	9.12 13.29	irregular rhombohedric brown plates	75
10.	*m*-toluidine	I	682.4	Co 8.63 N 12.31	8.45 12.23	thin irregular brown plates	80
11.	*m*-toluidine	NCS	613.6	Co 9.60 S 5.22	9.96 5.10	yellow thin acicular cryst. aggregate	70
12.	*m*-toluidine	ClO$_4$	655	Co 8.99	8.92	acicular cryst. aggregate	85
13.	*p*-toluidine	Cl	591	Co 9.97 N 14.22	9.95 14.17	red-brown long prisms	60
14.	*p*-toluidine	Br	635.5	Co 9.27 N 13.22	9.20 13.27	brown rectangular prisms	65
15.	*p*-toluidine	I	682.4	Co 8.63 N 12.31	8.45 12.59	dark red rhombohedric cryst.	70
16.	*p*-toluidine	NCS	613.6	Co 9.60 S 5.22	9.72 5.27	brown thin acicular cryst. aggregate	65
17.	*p*-toluidine	ClO$_4$	655	Co 8.99	8.86	long, yellow-brown needles	85
18.	*o*-ethylaniline	I	710.5	Co 8.29 N 11.82	8.15 11.70	brown, irregular hexagonal plates	65
19.	*p*-ethylaniline	Cl	619.1	Co 9.52 N 13.57	9.36 13.61	brown prisms	60
20.	*p*-ethylaniline	I	710.5	Co 8.29 N 11.82	8.33 11.64	dark brown thin prisms	70

No.	Am	X	Mol. weight	Analysis		Appearance	Yield %
				Calcd.	Found		
21.	*p*-ethylaniline	NCS	641.7	Co 9.18 S 4.99	9.06 4.78	yellow-brown, irregular prisms	50
22.	*o*-anisidine	Cl	623	Co 9.46 N 13.49	9.33 13.54	fibrous brown prisms	45
23.	*o*-anisidine	NCS	645.6	Co 9.11 S 4.96	9.43 4.87	long, brown prisms	30
24.	*o*-anisidine	I	714.4	Co 8.25 N 11.76	8.14 11.82	brown rhombohedric prisms	70
25.	*o*-anisidine	ClO_4	687	Co 8.57	8.39	long, thin yellow-brown needles	75
26.	*p*-anisidine	$Cl \cdot 2H_2O$	659	Co 8.95 N 12.75	9.11 12.86	brown needles	85
27.	*p*-anisidine	Br	667.5	Co 8.83 N 12.59	8.70 12.30	brilliant dark-brown prisms	75
28.	*p*-anisidine	I	714.4	Co 8.25 N 11.76	8.60 11.50	dark-brown needles	80
29.	*p*-anisidine	NCS,H_2O	664	Co 8.87 S 4.82	8.82 4.77	yellow-brown, thin needles	77
30.	*p*-anisidine	ClO_4	687	Co 8.57	8.47	yellow-brown thin needles	80

"Cy" = $C_6H_9N_2O_2$

Analysis. The complexes were digested with conc. H_2SO_4 and a few drops of conc. HNO_3. The solution was neutralized with CH_3COONa. Cobalt was determined complexometrically in the presence of *Murexide*, nitrogen by DUMAS' method, and sulphur gravimetrically, as $BaSO_4$.

The analysis data, a short characterization of the products, and yields are given in Table IV.

The thermogravimetric analysis was made with a thermobalance, worked out on the basis of literature data [8]. The heating rate was $q = 10$ °C/min.

SUMMARY

There were synthetized over 30 new Co (III) nioximine complexes and their behaviour was studied by thermogravimetric analysis. In the case of chlorides, bromides, iodides and thiocyanates the formation of the nonelectrolytic intermediate $[Co(Cy)_2Amin\ X]$ was observed. By HOROWITZ and METZGER's method the activation energies and entropies of the substitution reaction which leads to the formation of this intermediate were calculated. A hypothesis concerning the mechanism of this reaction is suggested.

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ISOTOPIC EFFECTS ON VAPOUR PRESSURE, II*

EFFECT OF DEUTERIUM SUBSTITUTION ON THE VAPOUR PRESSURES OF METHANOL AND ETHANOL

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Introduction

The vapour pressure of H_2O, at moderate temperatures more volatile than D_2O, is known to be equal to that of the latter at 225°C, while above this, so-called "cross-over" temperature D_2O becomes the more volatile of the two compounds [1]. A similar phenomenon in the isotopic effect has been reported for water below freezing temperatures by Johannin and Johannin Gilles. However, the fallaciousness of this, also theoretically not interpretable statement, has been shown in an earlier paper [2].

In order to obtain further information about the nature of the isotopic effect on vapour pressure, it was thought of interest to study in addition to water, some other compounds linked by hydrogen bonds. Alcohols presented themselves in the first place for use as models. Vapour pressure measurements were performed on the various derivatives of methanol, thus on CH_3OD first by Beersmans and Jungers [3], then reproduced by Efremov *et al.* [4]. Rabinovich and his co-workers [5] determined, in addition, the vapour pressure of C_2H_5OD. However, temperature dependence and cross-over studies require precise measurements over a more extended range of temperatures than that covered by the authors referred to. Some of the earlier results already reported [6, 7] will be now presented in a form completed with data from later and repeated experiments and discussed in more detail.

Experimental technique and results

Several methods have been proposed for the production of deuterated derivatives from methyl and ethyl alcohol, among which hydrolysis of sodium alcoholates in heavy water proved to be the most convenient [8]. Alcohols, purified by distillation were converted into sodium alcoholates and these were hydrolyzed in 99,9 atomic % heavy water, and purified in a semi-micro rectifier into which some metallic sodium was added to keep it free from water. The data of materials and products are listed in Table I.

The vapour pressures of the deutero alcohols were compared with those of the corresponding alcohols of natural isotopic abundance. At lower temperatures the vapour pressures up to

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* Part I. [2].

Table I

Data of compounds used in the experiments

	D atom per cent	$n_D^{20°}$	Boiling point °C
Methanol	natural	1.3288	64.8
Methanol-d	97	1.3274	65.6
Ethanol	natural	1.3611	78.4
Ethanol-d	99	1.3606	79.0

a difference of 2 mm Hg were compared using the differential manometer already described [2], the membrane of which is a 0.3 mm thick, concentrically corrugated plate. The sensitivity of the membrane permits to measure differential pressures of the order of 0.005 mm Hg.

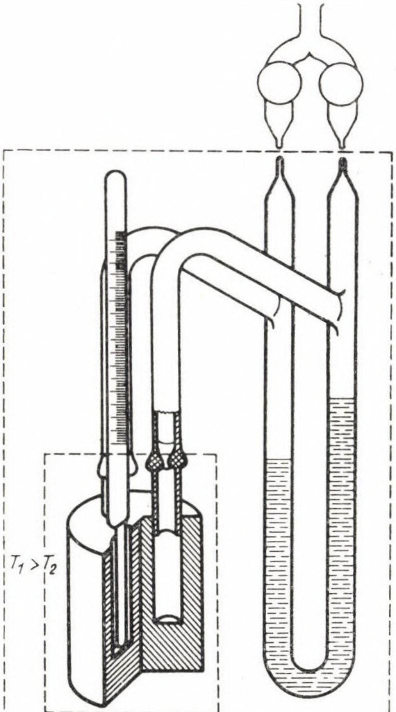

Fig. 1. Apparatus used for the measurement of vapour pressure differences higher than 2 mm Hg

The pressure differences above 2 mm Hg were measured with a differential mercury manometer apparatus. The difference between the mercury levels in the 18 mm diameter U-shaped tube could be read with a cathetometer to 0.05 mm accuracy. The readings expressed by the differences of the height of mercury levels have been corrected to 0° C. Reduction of mercury

Table II

Results for CH_3OH-CH_3OD

t °C	P_{CH_3OH} mm Hg	ΔP mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln\alpha$
—22.3	6.0	0.576	10.094	
20.3	7.0	0.665	9.985	
16.8	9.0	0.804	9.359	
15.5	10.0	0.875	9.159	
13.9	11.0	0.949	9.023	
12.6	12.0	1.032	8.995	
11.4	13.0	1.101	8.848	
10.5	14.0	1.173	8.746	
9.5	15.0	1.236	8.601	
8.6	16.0	1.312	8.555	
7.7	17.0	1.374	8.426	
6.8	18.0	1.445	8.371	
6.0	19.0	1.507	8.260	
5.1	20.0	1.562	8.131	
4.4	21.0	1.638	8.122	
3.7	22.0	1.709	8.085	
2.9	23.0	1.759	7.956	
2.3	24.0	1.805	7.818	
1.7	25.0	1.855	7.705	
1.0	26.0	1.924	7.791	
—0.4	27.0	1.998	7.687	
+0.2	28.0	2.036	7.567	
0.7	29.0	2.082	7.447	
1.4	30.0	2.121	7.325	
5.0	39.0	2.70	7.047	
6.0	42.0	2.90	7.160	
6.0	42.0	2.90	7.160	
7.4	45.0	3.05	6.934	
8.0	47.0	3.10	6.775	
8.9	49.6	3.30	6.888	
+9.0	50.0	3.25	6.720	
10.0	53.2	3.30	6.402	
11.0	56.4	3.60	6.598	
11.1	56.9	3.55	6.439	
11.5	58.0	3.75	6.683	
12.0	59.7	3.70	6.402	6.339
12.6	62.0	3.70	6.158	6.096

t °C	P_{CH_3OH} mm Hg	ΔP mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
13.0	63.3	3.90	6.363	6.298
13.1	63.7	3.90	6.317	6.252
13.5	65.2	4.00	6.335	6.269
14.4	68.5	4.10	6.176	6.110
15.0	71.0	4.20	6.100	6.094
15.0	71.0	4.25	6.176	6.170
15.9	75.0	4.40	6.045	5.976
16.0	79.8	4.55	5.874	5.805
17.4	81.3	4.70	5.960	5.888
18.0	84.0	4.85	5.951	5.878
18.5	86.0	4.90	5.865	5.791
19.0	88.6	5.05	5.865	5.790
20.0	93.8	5.20	5.704	5.629
22.5	106.5	5.80	5.600	5.519
28.0	142.8	7.10	5.098	5.010
31.4	170.0	7.95	4.794	4.701
32.1	176.0	8.25	4.804	4.709
32.6	180.0	8.35	4.746	4.650
32.6	180.0	8.40	4.785	4.688
33.1	184.5	8.70	4.794	4.696
33.5	189.0	8.80	4.765	4.666
33.6	190.0	8.80	4.746	4.647
35.6	209.0	9.30	4.555	4.454
36.0	213.0	9.50	4.564	4.462
36.4	217.0	9.65	4.546	4.442
37.4	228.0	9.90	4.440	4.335
40.1	260.0	10.85	4.258	4.148
40.5	265.0	11.15	4.297	4.184
41.1	272.0	11.35	4.258	4.145
43.0	297.0	12.10	4.164	4.046
45.0	312.0	12.80	4.191	4.066
45.3	315.0	13.00	4.209	4.083
48.3	360.0	14.10	4.000	3.870
49.8	401.1	14.75	3.749	3.622
49.9	403.0	14.80	3.740	3.613
50.0	407.0	14.85	3.740	3.613
50.0	407.0	14.95	3.765	3.638
50.5	414.0	15.30	3.767	3.637

t °C	P_{CH_3OH} mm Hg	ΔP mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
52.3	446.0	15.90	3.634	3.503
52.5	450.0	16.05	3.634	3.502
53.1	462.0	16.45	3.625	3.491
53.5	470.0	16.60	3.802	3.661
54.6	492.0	17.30	3.576	3.439
55.0	500.0	16.80	3.417	3.285
57.6	558.0	18.45	3.362	3.224
58.0	569.0	18.50	3.304	3.167
60.0	615.0	19.65	3.217	3.077
60.0	615.0	19.30	3.187	3.048
60.7	634.0	20.00	3.208	3.067
62.7	692.0	21.00	3.083	2.941
63.2	707.0	21.50	3.093	2.949
65.0	763.0	21.42	2.846	2.709
65.1	765.0	22.35	2.966	2.822
65.5	776.0	22.15	2.897	2.755
70.0	930.0	23.54	2.563	2.424
75.0	1110	25.89	2.360	2.218
80.0	1320	28.25	2.162	2.018
85.0	1580	30.60	1.955	1.813
90.0	1870	31.78	1.715	1.579
95.0	2200	34.02	1.556	1.421
100.0	2600	35.30	1.365	1.237
105.0	3000	36.02	1.206	1.084
110.0	3500	36.84	1.057	0.942
115.0	4100	36.60	0.895	0.790
120.0	4700	35.66	0.760	0.662

height to latitude 45° and to sea-level can be neglected, the correction being by 2 orders of magnitude smaller than the experimental error. Similarly to the set-up with membrane manometer, a copper block with two symmetrically drilled holes joined by metal to glass soldering to the glass tubing of the manometer was used as equilibrium vessel. The samples were introduced into the system evacuated to 10^{-6} mm Hg directly from the ampoules by soldering their seals to the glass tube and transferred by distillation into the equilibrium vessel. The measuring set-up could be operated up to a pressure of 8 atmospheres. The temperature was measured by mercury thermometer with a scale calibrated to 0.1°C accuracy. The entire apparatus was kept immersed in liquid thermostat exceeding by 1—2°C the temperature of the equilibrium vessel. The schematic drawing of the assembly is shown in Fig. 1.

The difference in vapour pressure could be measured by these set-ups for CH_3OH and CH_3OD at temperatures from —20° to 120°C, for C_2H_5OH and C_2H_5OD from —15° to 140°C. The measured values are listed in Tables II and III. Since the data reported on the vapour pressure of methanol show some discrepancy e.g. even in text books [9, 10, 11, 12, 13], also the temperature dependence of the vapour pressure was measured for both alcohols. The values obtained for

Table III

Results for C_2H_5OH *and* C_2H_5OD

t °C	$p_{C_2H_5OH}$ mm Hg	Δ P mm Hg	$10^2 \ln \frac{p_H}{p_D}$	$10^2 \ln \alpha$
−14.5	4.0	0.384	10.094	
11.4	5.0	0.465	9.760	
9.5	6.0	0.534	9.322	
7.3	7.0	0.602	8.995	
5.3	8.0	0.688	8.995	
3.9	9.0	0.765	8.885	
2.2	10.0	0.810	8.454	
−0.7	11.0	0.872	8.261	
+0.5	12.0	0.940	8.159	
1.7	13.0	1.019	8.169	
3.1	14.0	1.084	8.113	
4.0	15.0	1.148	7.957	
4.8	16.0	1.189	7.724	
5.7	17.0	1.244	7.604	
6.8	18.0	1.323	7.632	
7.5	19.0	1.372	7.494	
8.5	20.0	1.424	7.393	
9.1	21.0	1.485	7.335	
9.7	22.0	1.547	7.289	
10.5	23.0	1.601	7.215	
11.2	24.0	1.656	7.148	
11.9	25.0	1.698	7.029	
12.5	26.0	1.747	6.953	
13.2	27.0	1.785	6.858	
13.7	28.0	1.842	6.805	
14.2	29.0	1.908	6.805	
14.8	30.0	1.944	6.702	
15.4	31.0	1.990	6.637	
15.8	32.0	2.022	6.534	
16.2	33.0	2.056	6.430	
16.7	34.0	2.108	6.402	
17.3	35.0	2.198	6.485	
24.9	55.6	3.10	5.744	
29.5	72.2	3.85	5.403	
32.0	82.8	4.30	5.327	5.271
35.7	102.3	4.80	4.804	4.751
37.5	112.6	5.30	4.822	4.768

t C°	$P_{C_2H_5OH}$ mm Hg	ΔP mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
40.7	133.1	5.85	4.498	4.441
42.0	142.0	6.10	4.392	4.332
44.8	163.5	6.78	4.240	4.179
46.4	177.0	7.10	4.095	4.033
48.9	200.0	7.80	3.980	3.915
51.0	224.0	8.40	3.827	3.760
53.5	252.0	8.97	3.625	3.556
56.1	283.0	9.86	3.547	3.474
58.8	321.0	10.50	3.325	3.252
59.3	327.0	10.70	3.325	3.251
60.0	338.0	11.60	3.353	3.278
63.0	387.0	11.62	3.044	2.969
64.6	416.0	12.40	3.024	2.947
66.1	440.0	12.65	2.927	2.849
68.1	482.0	13.20	2.982	2.704
68.4	487.0	13.46	2.800	2.720
70.0	522.0	13.65	2.655	2.577
70.1	528.0	13.72	2.635	2.557
71.6	557.0	14.40	2.655	2.545
72.6	582.0	14.65	2.556	2.475
72.9	590.0	14.75	2.538	2.457
74.0	615.0	15.35	2.529	2.438
75.0	640.0	15.12	2.390	2.316
75.6	657.0	15.28	2.363	2.285
77.1	697.0	15.67	2.275	2.198
77.3	704.0	15.70	2.254	2.177
78.3	705.0	15.90	2.284	2.205
78.9	750.0	16.10	2.176	2.100
88.5	1130	19.80	1.607	1.535
95.5	1440	19.40	1.390	1.315
102.0	1750	20.00	1.149	1.074
102.3	1830	19.05	1.047	0.978
106.6	2100	21.00	1.005	0.930
114.6	2740	18.50	0.677	0.611
115.8	2840	20.00	0.707	0.635
119.0	3100	13.00	0.420	0.357
120.0	3220	14.60	0.454	0.401
121.5	3380	14.90	0.443	0.389

t °C	$P_{C_2H_5OH}$ mm Hg	ΔP mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
122.6	3500	11.30	0.323	0.283
124.0	3640	11.80	0.324	0.283
124.5	3700	10.00	0.271	0.235
126.0	3900	12.60	0.323	0.279
127.0	4200	9.70	0.231	0.197
129.5	4300	7.80	0.182	0.155
132.8	4700	6.50	0.138	0.116
134.0	4820	+2.50	+0.052	+0.044
135.0	4810	+0.70	+0.020	+0.017
136.0	5100	0.00	0.000	0.000
138.0	5400	−3.85	−0.071	−0.059
139.0	5520	−5.45	−0.099	−0.081
140.2	5700	−7.90	−0.139	−0.114

methanol are in agreement with those given in the manual of STULL [9] showing not more than 1 per cent deviation from the latest experimental data [13]. Also the values measured on ethanol are in agreement with the data of [9].

The comparison of the measured values with those obtained by other authors is to be seen in Fig. 2. The data for methanol are in fair agreement (within 8—15%) with the values

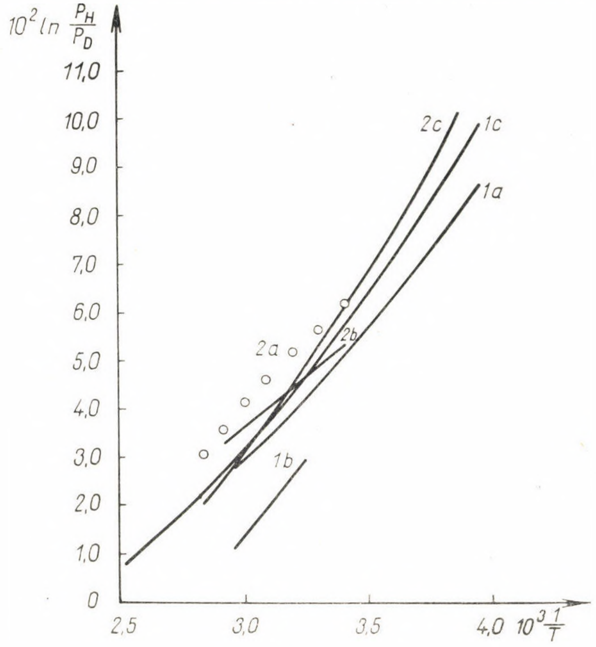

Fig. 2. Comparison of vapour pressure data for the isotopic pairs $CH_3OH—CH_3OD$ and $C_2H_5OH—C_2H_5OD$ gained by various authors: 1a) BEERSMANS and JUNGERS [3]; 1b) EFREMOV *et al.* [4]; 1c) this paper; 2a) RABINOVICH [5]; 2b) RABINOVICH [14]; 2c) this paper

reported by **Beersmans** and **Jungers** [3] and **Rabinovich** [5] which differ from those obtained by **Efremov** *et al.* [4]. It is also to be seen that in the case of ethanol there is a considerable deviation between the equation given by **Rabinovich** [14] and his experimental results.

The cross-over temperature could be directly measured in the case of ethanol and was found to be 136 ± 2°C.

Discussion

In lack of a statistical and thermodynamical equation of state for the liquid phase, it is impossible for the time being to evaluate accurately the isotopic effect on the vapour pressure of polyatomic molecules. At moderate temperatures, as shown by **Bigeleisen** [15, 16] the temperature dependence of the isotopic effect on the liquid-vapour equilibrium can be well approximated by the formula

$$\ln \alpha = \ln \frac{(H/D)_v}{(H/D)_l} = \frac{A}{T^2} - \frac{B}{T} \tag{1}$$

where α is the separation factor, $(H/D)_v$ and $(H/D)_l$ are the ratios of atomic fractions in the vapour and liquid phases, respectively. A is associated with the hindered molecular translation and rotation, if as usually, their frequencies (ν) satisfy the condition

$$\frac{h\nu}{kT} \ll 2\pi$$

In this case

$$A = \frac{1}{24}\left(\frac{h}{k}\right)^2 \sum (\nu_H^2 - \nu_D^2) \tag{2}$$

B is connected with shifts in the zero point energies of the internal vibrations on condensation, when usually for all ν

$$\frac{h\nu}{kT} > 2\pi$$

and thus

$$B = \frac{h}{2k}\left[\left(\sum \nu_{Hv} - \sum \nu_{Hl}\right) - \left(\sum \nu_{Dv} - \sum \nu_{Dl}\right)\right] \tag{3}$$

where h is the Planck constant, k is the Boltzmann constant, while indices H and D represent the molecules containing hydrogen and deuterium, v and l the vapour and liquid phases, respectively.

Taking the mixtures of the isotopic compounds in both the liquid and vapour phases to be ideal and assuming the vapour to behave as an ideal gas, we can write

$$\alpha_{id} = \frac{P_H}{P_D} . \tag{4}$$

The vapour phase cannot be approximated in the entire range of temperatures covered by present measurement by the formula for an ideal gas. Using the virial-equation of state for a real gas the pressure ratios and the separation factor can be related [15], as

$$\begin{aligned} \ln \frac{P_H}{P_D} = \ln \alpha - (RT)^{-1} \int_{V_D}^{V_H} P_H \, dV + (RT)^{-1} (P_H V_H - P_D V_D) - \\ - \left| \left(B_0 P + \frac{1}{2} C_0 P^2 + \frac{1}{3} D_0 P^3 + \ldots \right)_H - \right. \\ \left. - \left(B_0 P + \frac{1}{2} C_0 P^2 + \frac{1}{3} D_0 P^3 + \ldots \right)_D \right| \end{aligned} \tag{5}$$

where V_H and V_D are the molar volumes in the liquid phases of the compounds containing the isotopic species, H and D, respectively,

B_0, C_0, D_0 are virial coefficients,

R is the gas constant.

Let us see now the correction terms in equation (5). The value of $(RT)^{-1} \int_{V_D}^{V_H} P_H dV$, which for e.g. C_2H_5OD at 50°C amounts to 0.1% of the logarithm of the separation factor, can be neglected. $(RT)^{-1}$ $(P_H V_H - P_D V_D)$ can be evaluated from the density versus temperature curves [17] for heavier and light alcohols. Since, for *e.g.* deuteroethanol at 50°C this value is only 0.06% of the logarithm of the separation factor and even at higher temperatures does not exceed 0.5%, it also can be neglected.

The terms containing virial coefficients may become important above certain temperatures. As a result of quantum effects, a difference is expected to arise between the virial coefficients of isotopic pairs. No relevant experimental data being available, this difference can be estimated by making use of the STOCKMAYER—ROWLINSON method [18, 19]. Assuming the dipole moments of the isotopic molecular pairs to be virtually equal as it is suggested by RABINOVICH [14] and HALEVI *et al.* [20] and also experimentally evident in the case of H_2O and D_2O [21], as well as considering that the difference in dispersion interactions, evaluated from RABINOVICH's measurement [22] is $\varepsilon_H/\varepsilon_D = 1.0054$, where ε_H and ε_D are the dispersion interaction energies for methanol and deuteromethanol, respectively, the absolute value of the second virial coefficients *e.g.* for deuteromethanol at 120°C should not exceed by more than 1% that of methanol. Thereupon taking the virial coefficients of the two isotopic varieties to be equal, calculations were carried out according to the following equation

$$\ln \alpha \simeq \ln \frac{P_H}{P_D} + B_{0H}(P_H - P_D) + \frac{1}{3} D_{0H}(P_H^3 - P_D^3) \tag{5a}$$

For both methanol [23—25] and ethanol [25, 26] the virial coefficients have been already determined by various methods. The data covering the widest range of temperatures reported and therefore the most adequate for our calculations, are those of KRETSCHMER and WIEBE [25] who give the equation of state for the vapour phase of methanol and ethanol in terms of the second and fourth virial coefficients (Table IV). The values of ln α computed from expression (5a) and the measured values of the differences in vapour pressures are listed in Tables II and III. (At lower temperatures, when the correction does not exceed 1%, ln α is taken to be equal to the logarithm of the ratio of vapour pressures.) It can be seen that the deviation from the ideal induces in the case of methanol at 120°C a correction of about 13%.

The equation (1) was fitted by the method of least squares to the experimental data corrected on basis of the equation for alcohol vapours. While in the case of methanol the equation with the constants obtained from the fit yields a fairly good approximation to the experimental data, the values measured for ethanol in a wider range of temperatures cannot be approximated by the same values of A and B in the entire range covered by the measurement. The reason for this is that in equations (2) and (3) obtained by power expansion in which the higher order terms are neglected, give a fair approximation only if we have frequencies $h\nu/kT \ll 2\pi$ in the formula for A and $h\nu/kT > 2\pi$ for B. These values, however, may change with the temperature and the condition $h\nu/kT > 2\pi$ is probably not satisfied in the case of ethanol for B over the entire range of temperatures under investigation. If we divide the curve for ethanol into two sections, one below, the other above the boiling point, either of the sections can be individually well described by a relation of the form (1). The values of A and B computed in this way from experimental data by the least square method are listed in Table V.

Table IV

Virial coefficients for methanol and ethanol used in the calculation [25]

	$PV/RT = 1 + B_0P + D_0P^3$	
	RTB_0 ml/mol	RTD_0 ml/mm^2 mol
CH_3OH	$-100-2.148 \exp(1986/T)$	$-1.445 \cdot 10^{-17} \exp(10{,}750/T)$
C_2H_5OH	$-290-0.284 \exp(2730/T)$	$-1.00 \cdot 10^{-5}-7.58 \cdot 10^{-18} \exp(11{,}144/T)$

Table V

Constants of equation (1) and the cross-over temperatures

		$A \cdot 10^{-2}$	$\sigma_A \cdot 10^{-2}$	B	σ_B	cross-over temp. °C	
						extrapolated	experimental
CH_3OH-CH_3OD		160.39	0.48	38.03	0.17	148.5	—
$C_2H_5OH-C_2H_5OD$	between −15 and +78°C	183.43	0.49	44.45	0.12	135.4	136±2
	between 78 and 140°C	179.6	5.9	43.96	0.22		

It follows from equation (5) that if at the cross-over temperature the differences between the terms containing the molar volumes and those between the virial coefficients are neglected, we have

$$\alpha_{T_{c.o.}} \simeq \left(\frac{P_H}{P_D}\right)_{T_{c.o.}} = 1\,. \tag{6}$$

The temperature dependences of ln α and ln P_H/P_D in the vicinity of the cross-over temperature for the ethanol-deuteroethanol system are shown in Fig. 3. It is apparent that the relationship is similar to that observed for the

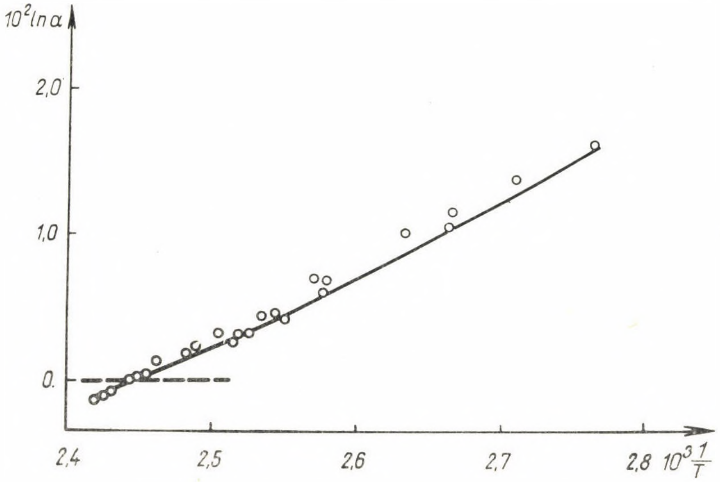

Fig. 3. Comparison of $\ln \frac{P_H}{P_D}$ (points) and ln α (full line) near the cross-over temperature in the $C_2H_5OH-C_2H_5OD$ system

H_2O—HDO system by **Merlivat** *et al.* [27] who used the experimentally determined values of α to compute the ratio of the H_2O to HDO vapour pressures.

The data can be used for the evaluation of the difference in the heats of vaporization of isotopic varieties from the Clausius—Clapeyron equation

$$\Delta H_H - \Delta H_D = RT^2 \frac{d \ln \frac{P_H}{P_D}}{dT} \tag{7}$$

where ΔH_H and ΔH_D are the heat of vaporization of the compounds with hydrogen and deuterium content, respectively. The difference in the heats of vaporization was calculated from spectroscopic data at $T = 298.2°K$ using the method suggested by **Rabinovich** [14] who applied it in the case of methanol. The effect of the deuterium substitution on the vibrations of the OH group is taken into account only, and all vibrations are considered as harmonic. The details of the calculations have been given in another paper [28]. The results are summarized in Table VI. The differences in the heats of vaporization calculated by this method are found to agree with the values computed from the experimental data in the case of ethanol only.

Similar investigations concerning other alcohols are in progress.

Table VI

Differences in the heats of vaporization at 25°C

	$(\Delta H_D - \Delta H_H)$ cal/mol	
	experimental	calculated
CH_3OH-CH_3OD	135 ± 10	77
$C_2H_5OH-C_2H_5OD$	157 ± 10	142

SUMMARY

The differences between vapour pressures of CH_3OH and CH_3OD, and those of C_2H_5OH and C_2H_5OD have been determined experimentally in a wide range of temperatures. On the basis of the experimental data and the virial equations for the vapours of alcohols the separation factor (α) for distillation of the isotopic mixtures has been calculated. The temperature dependence of α can be given with good approximation by **Bigeleisen**'s equation, $\ln \alpha = A/T^2 - B/T$, where A and B are constants in a definite range of temperature. The cross-over temperatures above which the heavier molecule becomes more volatile, and the differences in the heats of vaporization, have also been determined.

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ELECTRON MICROSCOPICAL INVESTIGATIONS ON SOLS WITHOUT STRUCTURAL CHANGE

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Introduction

The greatest problem in the study of colloid systems by electron microscope is the preparation of the specimen. The coagulations during drying cause an increase in particle size in case of sols and a change of structure in case of gels. From the present preparation methods the freeze-drying seems to be the most proper one. It is known, however, that coagulation may take place even during freezing. But the probability of appearance of coagulation decreases with the increase of the rate of freezing [1].

Freeze-drying apparatus and methods for preparation of specimens for electron microscopy are described by several authors. The method of WILLIAMS [2], STEERE [3], HALL [4] and TOKIO NEI [5] seemed to be the most suitable to the authors' purpose. With the method of Tokio Nei bacteria were studied here and the results obtained were substantially identical with results given by him [6]. During preparatory tests, care was taken that the size and distribution of particles should not change even in case of colloid systems highly sensitive to freezing coagulation. It was found, that though the above-mentioned authors employed their methods and apparatus with success, these methods were not entirely suitable for the present objects owing to one of the following causes. The rate of drying in case of several apparatus was relatively low. The methods did not ensure in every case a high enough freezing rate. One could not study directly the specimens after freeze-drying only after secondary operations, which might cause errors and in case of replica the resolution of the replica was lower than that of a modern electron microscope. The preparative operations were not mild enough and some of them were also complicated.

Considering this the authors' purpose was to prepare such an apparatus and to work out such a method which fulfil the theoretical and practical requirements of freeze-drying (high freezing and sublimation rates) and at the same time require only a few and mild preparative operations. The employed apparatus should be simple and should ensure the utilization of the advantages of the modern electron microscopes of high resolving power.

The apparatus and the preparation of the specimen

Specimens were prepared in the drying head shown in Fig. 1. Into the vessel protrudes, by a ground joint, a freezing trap fed with liquid nitrogen. On the bottom of the vessel an aluminium block is placed. With the shape of the aluminium block the appropriate metal vaporization angle is ensured. The upper rim of the vessel was ground to which a cover was attached with a rubber seal in which were mounted the current feed of the palladium vaporized and the thermometer joint. The temperature of the aluminium block was measured by the thermometer.

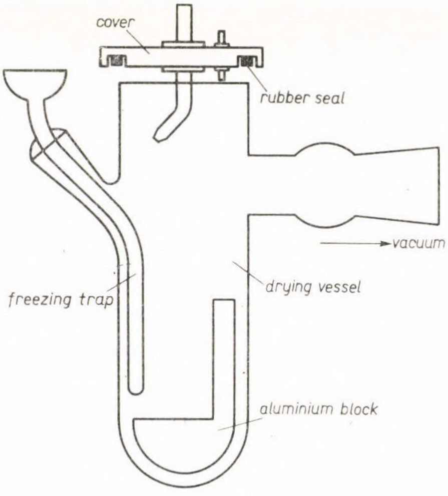

Fig. 1

Even from this schematic description it is obvious that, by the choice of the shape and dimensions of the freeze drying head, the requirements expressed by the Knudsen equation are fulfilled favourably. As it is known the sublimation rate according to KNUDSEN is

$$Q_r = \frac{4}{3}\sqrt{\frac{2\pi M}{RT}}\,\frac{V^3}{L}\,(P_a - P_b)$$

where M is the molecular weight of H_2O;
R is the gas constant;
T is the absolute temperature;
r is the radius of the tube in which the vapour moves from the sample to the trap;
L is the length of the tube in which the vapour moves from the sample to the trap;

P_a is the partial pressure of the water on the sample;
P_b is the partial pressure of the water on the trap.

From the equation follows that to obtain a high sublimation rate one has to choose a high r and a small L and the greatest P_a in comparison with P_b; the P_a pressure, which is determined by the temperature of the sample, can be controlled by the temperature of the coolant that surrounds the lower part of the freeze drying head.

From several preparation processes the following one gave the required result. The micro grids on the aluminium plate carrying a *Formvar*-carbon film with the specimen sprayed on it were inserted in liquid nitrogen. Meanwhile the aluminium block in the freeze drying head was also cooled to the temperature of liquid air. To avoid fogging, the drying head was evacuated to a pre-vacuum. After letting in dry air, the cover was taken off and the sample was placed on the aluminium block. After mounting the cover, the fore- and, later on the high-vacuum pumps were connected. Drying was finished after reaching the highest vacuum of the system. The dried specimen was vaporized with palladium in the drying head. The specimen prepared in this way is directly suitable to investigations in electron microscope.

To the experiments *Formvar*-carbon films were used with success. A film was prepared from a 0.2% *Formvar* solution by the usual method on which a 100—200 Å thick carbon layer was vaporized. It was found that the *Formvar*-carbon film was suitable only when the thickness ratio of the *Formvar*-carbon layers was about 1 : 2. If the necessary ratio was not adhered to the film shrinked and got torn.

Instead of the usual glass slide — on which is the micro grid with the supporting film — an aluminium plate was used to increase even by this the rate of freezing. The specimen was applied on to the supporting film with the aid of a spray. The optimum diameter of the drops was 20 μm. The freezing of such a small drop has the advantage — besides the high cooling rate — that the drop, in case of 2000-fold magnification, can be viewed as a whole in the picture area of the electron microscope and so the particle distribution in the drop is more easily observed. The attainment of the high enough freezing rate is marked by the permanence of the statistically homogeneous distribution of the particles. A further decrease of the dimensions of the drops is not useful because of the vaporization after the spraying.

The investigations were carried out by a *Tesla BS242A—D*, an *ELMMI—D* and a *Hitachi HU*—10 electron microscope.

Results

The experiments were carried out with sols of silver iodide and gold of small stability with which at an initial cooling rate of ~10°/sec a full coagulation takes place, *i.e.* after melting it gives a setting suspension. The dimensions of the coagulated particles are a few microns.

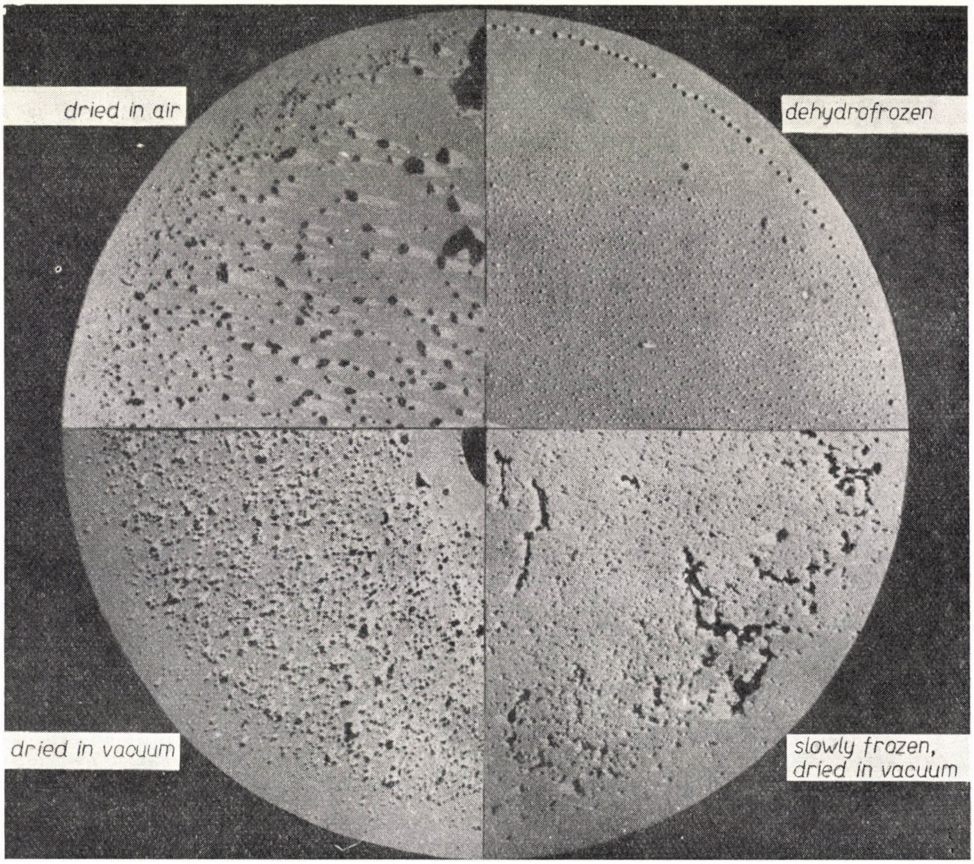

Fig. 2

The method shown above has been compared with other preparation methods. For this purpose four aluminium plates with micro grids were put beside one another and the specimen was sprayed on them. Of these samples one was dried in air, another in vacuum, another was dried by the above method and the last one was slowly frozen in the air at a temperature of —15°C and was dried in vacuum.

The results are shown in Fig. 2 (magnification: 10,000). The figures show considerable aggregation with the exception of the freeze dried specimen.

Aggregation forms only on the edges of the drops because during the time while carrying the specimen to the micro grid and freezing it there, there is a strong vaporization at the edges, the primary particles aggregate and mark the edge of the drop rather strictly. This can be avoided by spraying the sample only after cooling the aluminium plate carrying the micro grids to the temperature of liquid nitrogen. The electron micrograph remains unchanged as the cooling rate increases which proves that the method provides a high enough freezing rate and with it coagulation does not take place. The higher cooling rate was obtained by freezing in n-pentane cooled by liquid nitrogen. The initial cooling rate (+20 → 0°) in pentane was nearly thrice as high as that in liquid air.

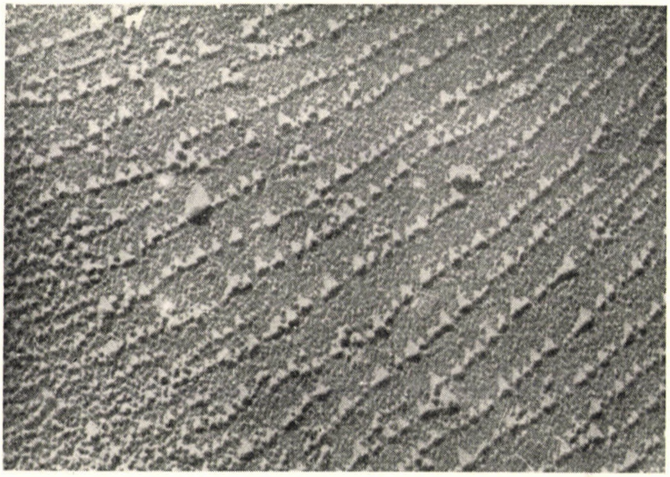

Fig. 3

If the cooling rate is not enough high in case of freezing of sols the electron micrograph shows a well-ordered structure. The formation of this structure is caused by the ice front moving from the edges towards the centre of the drop, this ice front is able to displace the particles in the liquid as it can be seen in Fig. 3 (magnification: 50,000) on a pattern of gold sol.

With the present method the initial statistically unaltered homogeneous distribution of the particles remains the same after its preparation. The only change is that the particles settle on the film and so one gets the projection on the film of their original distribution.

SUMMARY

A preparation method for electron microscopy and an apparatus for freeze drying are described which fulfil the theoretical and practical requirements of freeze drying. The apparatus is simple, easy to handle and the applied method ensures the utilization of the advantages of the electron microscopes with high resolving power.

Investigations were carried out with sols highly sensitive to freezing coagulation and it has been found that the method allows the preparation of a specimen without any change in its structure.

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ÜBER DEN EINFLUSS INAKTIVER OBERFLÄCHENBEREICHE AUF DEN DIFFUSIONSGRENZSTROM AN EINER ROTIERENDEN SCHEIBENELEKTRODE*

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An Festelektroden ist im allgemeinen mit heterogenen Oberflächen zu rechnen, d. h. die Durchtrittsrekation läuft nur an den aktiven Stellen ab. Es ist deshalb die dadurch verursachte Abweichung der Zudiffusion der Ausgangssubstanz zur Oberfläche von der Linearität zu berücksichtigen. Die Abweichung von der linearen Diffusion wird unter Umständen im gemessenen Diffusionsgrenzstrom zum Ausdruck kommen. Der Diffusionsgrenzstrom ist an der Scheibenelektrode genau berechenbar, deshalb wurde die Scheibenelektrode bei den Experimenten verwendet und liegt den theoretischen Erörterungen zugrunde.

Die Experimente zeigen, daß sich die nichtlineare Diffusion auf die Rührabhängigkeit des Diffusionsgrenzstromes folgendermaßen auswirken kann:

1. Im Diagramm $\frac{1}{I_{\text{diff}}}$ gegen $\frac{1}{u^{1/2}}$ erhält man eine Gerade, die nicht durch den Koordinatenursprung geht und aus deren Neigung gemäß Gleichung (5) der Diffusionskoeffizient berechenbar ist. Dieser funktionelle Zusammenhang wurde sowohl von Nagy und Mitarbeitern [1] als auch von uns [2] u. a. auch für verschiedene Systeme hoher Austauschstromdichte, wie Ferri-Ferro-Cyanid, für das eine vorgelagerte chemische Reaktion nicht in Frage kommt, gefunden (Abb. 1 und 2). Wir wollen den Zusammenhang, der durch eine Gerade im Diagramm der reziproken Stromdichte über der reziproken Wurzel aus der Umdrehungszahl der Elektrode gekennzeichnet ist, als reziproken Zusammenhang bezeichnen. Diese Gesetzmäßigkeit wird auch für eine gleichmäßig aktive Elektrode beobachtet, wenn nach Frumkin und Tedoradse [3] der eigentlichen Durchtrittsreaktion eine heterogene chemische Reaktion bzw. nach Koutecky und Lewitsch [4] eine sehr schnelle homogene Reaktion 1. Ordnung vorgelagert ist. Letzteres konnte bei dem System Ferro-Ferricyanid und anderen untersuchten Redoxysystemen, die dieser Gesetzmäßigkeiten an graphithaltigen Elektroden gehorchen, ausgeschlossen werden.

2. Sind die blockierten Stellen und die aktiven Bereiche in ihren Ausmaßen groß, verglichen mit der Diffusionsschichtdicke, so wird ein der Wurzel aus

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der Rührgeschwindigkeit proportionaler Grenzstrom beobachtet. Der mit Hilfe der LEWITSCH-Gleichung daraus berechenbare Diffusionskoeffizient, D, ist zu klein. Diese Gesetzmäßigkeiten haben wir bei der Reduktion von Sauerstoff und Wasserstoffperoxyd am paraffinierten Graphit beobachtet (Abb. 3). Die in Abb. 3 gezeigte unterschiedliche Neigung der Geraden konnte auf eine pH-abhängige Blockierung der Elektrode zurückgeführt werden [5]. Da der funktionelle Zusammenhang der gleiche ist, wie er der LEWITSCH-Beziehung für diffusionsbedingte Vorgänge entspricht, wollen wir diesen Bereich als den Quasi-LEWITSCH-Bereich bezeichnen.

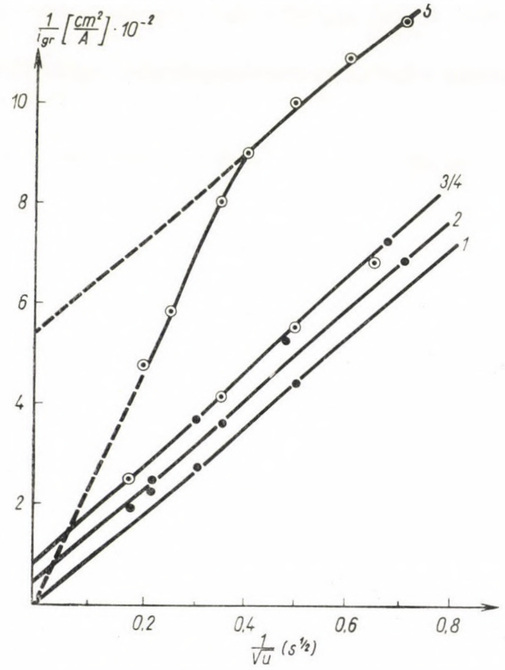

Abb. 1. Abhängigkeit des reziproken Grenzstromes der Oxydation von Kaliumferrocyanid an Diphenyl-Graphitelektroden von der Umdrehungszahl der Elektroden

$t = 20°$ C; 1 m KOH
$c_L = 1 \cdot 10^{-2}$ Mol/l $K_4[Fe(CN)_6]$
1 — Platin
2 — 5 Diphenyl-Graphit
2 — 50% Diphenyl
3 — 60% Diphenyl
4 — 70% Diphenyl
5 — 80% Diphenyl

Zur Berechnung des Diffusionsgrenzstromes nehmen wir als Modell kreisförmige, gleichmäßig auf der Oberfläche verteilte aktive Stellen an, die ringförmig von inaktiven Bereichen umgeben sind [1]. Über jeder aktiven Stelle können wir einen Zylinder errichten, dessen Länge (δ) der Diffusionsschichtdicke entspricht. Zur Lösungsseite hin ist seine gesamte Stirnfläche mit dem Radius r_2 vom Diffusionsstrom durchflossen, auf der Elektrodenoberfläche jedoch nur der aktive Teil mit dem Radius r_1 (Abb. 4). Die Zylinder berühren einander oder überlappen etwas wegen des zwischen ihnen übrig bleibenden Volumens. Die Aufgabe besteht darin, den Diffusionswiderstand eines solchen Zylinders zu bestimmen. Nagy und Mitarbeiter [1] haben darauf hingewiesen, daß ein mathematisch analoger Zusammenhang zwischen Diffusionsstrom und Konzentrationsgradient einerseits und elektrischem Strom und Potentialgradient andererseits besteht und haben mit Hilfe eines Analogrechners experimentell den elektrischen Widerstand des gegebenen Zylinders bestimmt. Sie fanden für den Widerstand

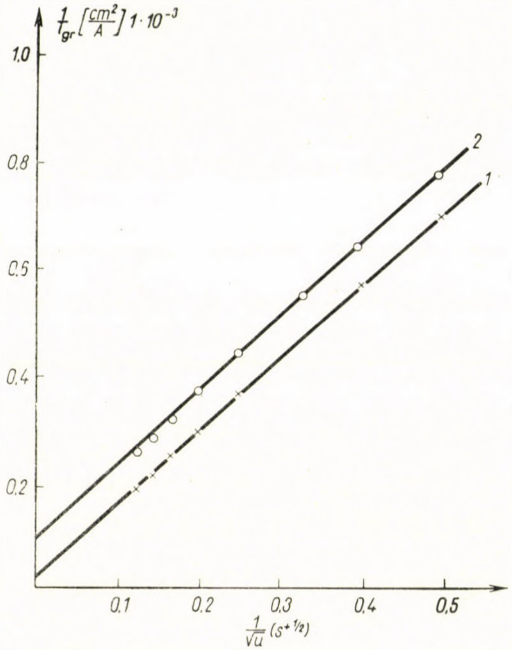

Abb. 2. Abhängigkeit des Grenzstromes der Manganat-VI-Oxydation von der Umdrehungszahl der Elektrode in den Koordinaten
i_{gr}^{-1}; $u^{-1/2}$
$t = 20°$ C; 1 *m* KOH
$c_L = 5{,}3 \cdot 10^{-3}$ *Mol*/l K_2MnO_4
1— Platin
2— Azobenzol-Graphit (60% Azobenzol)

$$R = \frac{1}{\varkappa \pi r_2^2}\left[p \cdot r_2 \left(\frac{r_2}{r_1} - 1\right) + l\right] \tag{1}$$

$\varkappa$ = spezifische Leitfähigkeit;
l = Länge des Zylinders;
p = eine Zahl, die sich aus den Messungen ergab.

SMYTHE [6] beschritt 1952 einen anderen Weg, indem er die Laplacesche Differentialgleichung für den zylindersymmetrischen Fall mit der Grenzbedingung, daß die kleinere Elektrode eine Äquipotentialfläche ist, und die Stromlinien am Zylindermantel mit dieser parallel verlaufen, löste. Seine Lösung für den Widerstand des Zylinder lautet

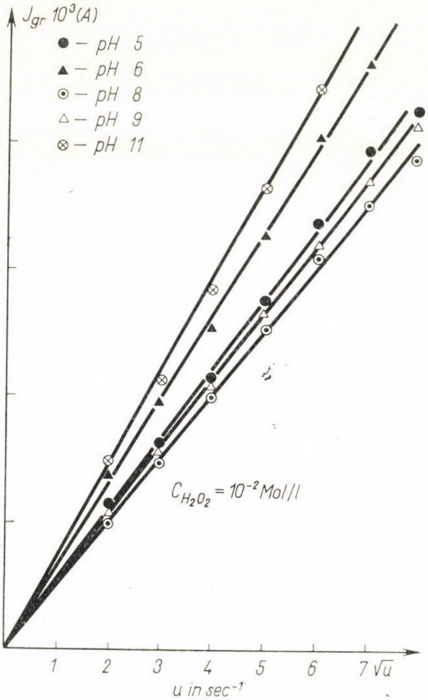

Abb. 3. Abhängigkeit des Grenzstromes der stationären Stromspannungskurven für die H_2O_2-Reduktion am paraffinierten Graphit von der Wurzel aus der Umdrehungszahl der Elektrode
$t = 25°\ C$
$c_L = 1 \cdot 10^{-2}$ *Mol*/l H_2O_2
u in s^{-1}

$$R = \frac{1}{\varkappa \pi r_2^2}\left(\sum_{n=1}^{n=\infty} A_n \left[\exp\left(-\frac{x_n}{r_2} l\right) J_0\left(\frac{x_n}{r_2}\cdot r\right) - 1\right] + l\right. \tag{2}$$

x_n sind die Nullstellen der Besselfunktion 1. Ordnung 1. Gattung (J_1). Für genügend lange Zylinder vereinfacht sich die Gleichung (2) zu

$$R = \frac{1}{\varkappa \pi r_2^2}\left(\left|\sum_{n=1}^{n=\infty} A_n\right| + l\right). \tag{3}$$

Für ΣA_n gibt SMYTHE eine Bestimmungsgleichung an, die gewissen Bedingungen genügt. Für drei Verhältnisse von r_1 zu r_2 hat SMYTHE die Summe der Koeffizienten $\frac{A_n}{r_2}$ unter Berücksichtigung der ersten 40 Glieder angegeben. Dieses Ergebnis wurde auf die Grenzstromdichte an einer rotierenden Scheibe übertragen, und man erhält für die Beziehung zwischen Stromdichte und Rührgeschwindigkeit nach SMYTHE, LANDSBERG und THIELE [2]

$$i_{gr}^{-1} = \frac{1{,}61\,\nu^{1/6}}{nF\,D^{2/3}\,c_L\,(2\pi)^{1/2}}\,u^{-1/2} + \frac{|\Sigma A_n \operatorname{tgh}(x_n/r_2 \cdot \delta)|}{nF\,D\,c_L}. \tag{4}$$

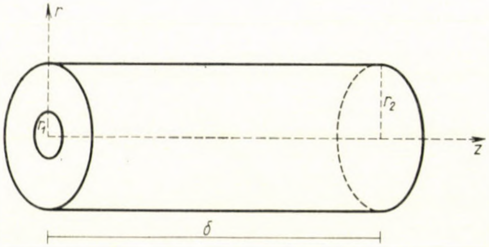

Abb. 4. Modell für den Diffusionszylinder über einem aktiven Bereich
r_1 = Radius des aktiven Bereiches
r_2 = Radius des Zylinders
δ = Diffusionsschichtdicke

1. Ist die Diffusionsgrenzschichtdicke groß, verglichen mit dem Radius der aktiven Stelle, so vereinfacht sich die Gleichung, da der tgh für große Argumente gegen 1 geht, und man erhält

$$i_{gr}^{-1} = \frac{1{,}61\,\nu^{1/6}}{nF\,D^{2/3}\,c_L\,(2\pi)^{1/2}}\,u^{-1/2} + \frac{|\Sigma A_n|}{nF\,D\,c_L}. \tag{5}$$

2. Für kleine Werte des Arguments kann der tgh(x) durch das Argument selbst ersetzt werden, und dieses ist der Diffusionsschichtdicke proportional bzw. der Wurzel aus der Umdrehungszahl der Elektrode umgekehrt proportional. In dem Quasi-LEWITSCH-Bereich besitzt die Gerade in der Auftragung Grenzstromdichte über der Wurzel aus der Umdrehungszahl eine kleinere Neigung als dem Produkt aus Diffusionskoeffizient und geometrischer Oberfläche der Elektrode entspricht.

Für die Reduktion von Wasserstoffperoxyd konnten wir bei unterschiedlichen Umdrehungszahlen den Übergang von einer Gesetzmäßigkeit in die

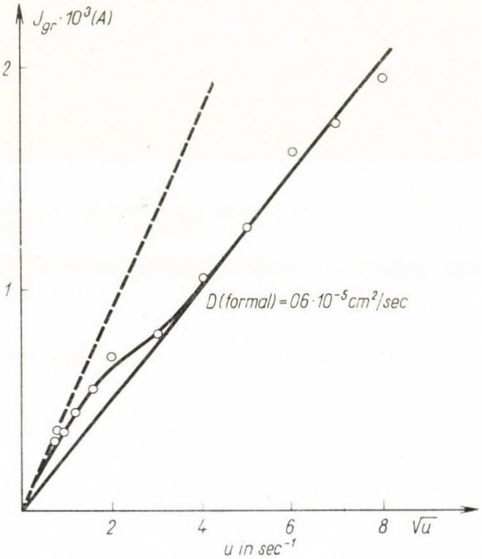

Abb. 5. Abhängigkeit des Grenzstromes der stationären Stromspannungskurve für die H_2O_2-Reduktion an einer speziell vorbehandelten paraffinierten Graphitelektrode von der Rührgeschwindigkeit

pH 7
$c_L = 6{,}2 \cdot 10^{-3}$ *Mol*/l H_2O_2
$t = 25°$ C

D(formal) wurde aus der LEWITSCH-Beziehung mit $n = 2$ und der geometrischen Elektrodenoberfläche berechnet. Die Tangente (gestrichelte Linie) hat immer noch eine zu kleine Neigung gegenüber der, die aus der LEWITSCH-Beziehung mit q(geometrisch) folgt

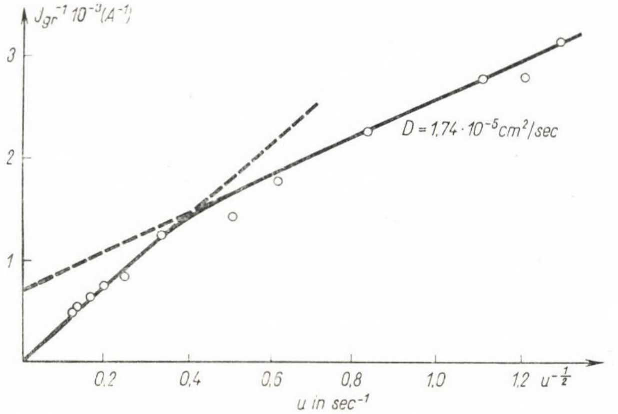

Abb. 6. Reziproke Auftragung der Meßwerte aus Abb. 5

andere beobachten (Abb. 5 und 6). Bei der Oxydation von Manganat an Azobenzol-Graphit-Elektroden beobachteten wir den reziproken Zusammenhang, wobei mit zunehmendem Azobenzolgehalt der Elektrode der Schnittpunkt der erhaltenen Geraden mit der Ordinate zunimmt. Das ist zu erwarten, denn ein zunehmender Azobenzolgehalt der Elektrode bedeutet eine Zunahme des Bedeckungsgrades der Elektrode. Abb. 7 zeigt den reziproken Wert des Ordinatenabschnittes, der in Stromdichteeinheiten angegeben ist, als Funktion des Azobenzolgehaltes der Elektrode, mit dem er erwartungsgemäß abnimmt.

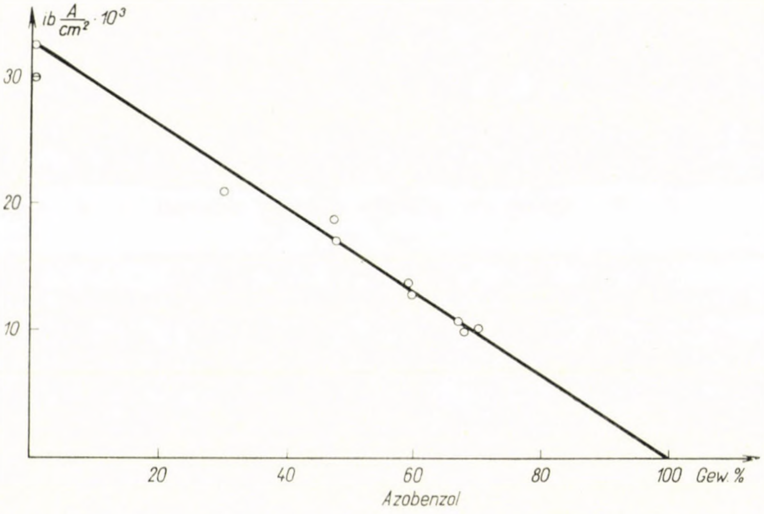

Abb. 7. Abhängigkeit der Stromdichte (i_b), die sich aus dem Ordinatenabschnitt bei der Auftragung der Meßwerte für den Grenzstrom der Manganat-VI-Oxydation in den Koordinaten i_{gr}^{-1}: $u^{-1/2}$ für $u = \infty$ ergibt, vom Azobenzolgehalt der Azobenzol-Graphitelektrode

$t = 20°$ C

$c_L = 2{,}85 \cdot 10^{-3}$ *Mol*/l K_2MnO_4

Für die Abschätzung der Größe der aktiven und inaktiven Bereiche gibt es verschiedene Möglichkeiten. Eine Methode läßt sich bei Mischelektroden mit einer inaktiven Komponente anwenden. Man untersucht, wie sich der Ordinatenabschnitt bei Änderung des Gehaltes an inaktiver Komponente ändert, den man der Änderung des Bedeckungsgrades näherungsweise gleichsetzen kann [2]. Dabei wird vorausgesetzt, daß auch bei der Elektrode aus zwei Komponenten die aktiven Stellen von einheitlicher Größe sind. Ist diese Methode nicht anwendbar, so könnten u. a. Messungen im reziproken wie auch im Quasi-LEWITSCH-Bereich Aufschluß geben, da wir dann zwei unterschiedliche Gleichungen für die beiden unbekannten Parameter erhalten. Man kann die Quasi-LEWITSCH-Beziehung erklären, indem man annimmt, daß für kleine δ/r_1 die Größe des Diffusionsgrenzstromes in der Hauptsache von der linearen Diffusion senkrecht zu den aktiven Stellen bestimmt wird, während der Beitrag der nichtlinearen Diffusion aus dem Volumen über den inaktiven Bereichen vernachlässigbar klein wird, da außerdem anzunehmen ist, daß durch die Konvektion über den inaktiven Bereichen der Anteil der nichtlinearen Diffusion zum Grenzstrom weiter vermindert wird. Es sollte dann die LEWITSCH-Beziehung gelten mit der aktiven Fläche an Stelle der geometrischen Fläche.

Die abschließenden allgemeinen Bemerkungen zu den entwickelten Vorstellungen weisen darauf hin, daß die hier gegebenen Beziehungen durch weitere Untersuchungen an Modellelektroden gestützt werden müssen:

1. Ein Mangel des Modells besteht in der Annahme kreisförmiger aktiver Bereiche. Das entspricht nicht den wirklichen Verhältnissen. Trotzdem zeigen die Versuche, daß der funktionelle Zusammenhang an wirklichen Elektroden gut wiedergegeben wird. Das liegt u. a. an der ausgeprägten Relaxation der Diffusion, die scharfe Spitzen ausgleicht. Am Rande des aktiven Bereiches liegt eine diffuse Zone nichtlinearer Diffusion.

2. Bei sich berührenden Kreisen wird ein gewisser Teil der Elektrodenfläche nicht erfaßt. Ob eine gewisse Überlappung der Kreise, die eine der Randbedingungen etwas verletzen würde, den wirklichen Verhältnissen besser gerecht wird, kann nur durch Versuche am Modell entschieden werden.

3. Der Stofftransport erfolgt in Wirklichkeit nicht nur durch reine Diffusion, sondern auch durch Konvektion. An der Elektrodenoberfläche sind allerdings die größten Abweichungen von der linearen Diffusion und der geringste Einfluß der Konvektion vorhanden.

4. Für den Beitrag der nichtlinearen Diffusion zum Betrage des Diffusionsgrenzstromes sollte nicht das Verhältnis δ/r_2, wie es bei der Ableitung von SMYTHE zum Ausdruck kommt, maßgebend sein, sondern das Verhältnis δ/r_1.

5. Da die Berechnung von SMYTHE für den zylindersymmetrischen Fall mit nur einem Modellzylinder durchgeführt wurde, ist die Übertragung seiner Berechnung auf die Diffusionsverhältnisse an einer teilweise blockierten Elektrodenfläche auch deshalb unsicher, weil bei hohen Blockierungsgraden die Konvektionsströmung die Stromdichte an den azentrischen aktiven Bereichen erhöhen kann.

Wir sind dabei, die hier aufgeworfenen Fragen an Modellelektroden zu untersuchen, und beabsichtigen, galvanostatische Messungen einzubeziehen, da bisherige Ergebnisse darauf hindeuten, daß das Modell auch hier anwendbar sein könnte.

ZUSAMMENFASSUNG

Es wird der Einfluß inaktiver Oberflächenbereiche auf die Rührabhängigkeit des Diffusionsgrenzstromes an einer Scheibenelektrode diskutiert. Mit Hilfe einer Modellvorstellung wird eine allgemeine Gleichung für die Rührabhängigkeit des Diffusionsgrenzstromes an einer teilweise blockierten rotierenden Scheibenelektrode gegeben, die qualitativ mit der experimentell ermittelten Abhängigkeit des Diffusionsgrenzstromes für die H_2O_2-Reduktion am paraffinierten Graphit, die Ferrocyanidoxydation und Manganatoxydation an graphithaltigen Elektroden von der Rührgeschwindigkeit übereinstimmt. Es werden abschließend einige allgemeine Bemerkungen über die Unzulänglichkeiten der Modellvorstellung für das vorliegende Problem gemacht.

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HYDANTOINS, THIOHYDANTOINS, GLYCOCYAMIDINES, XXV*

REARRANGEMENT OF THIOHYDANTOIN DERIVATIVES BY ALUMINUM CHLORIDE

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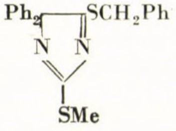
It has been previously [1, 2] reported that S-benzyl derivatives of 5,5-diphenylthiohydantoins can be debenzylated under relatively mild conditions by aluminum chloride or bromide. Under the conditions successfully used for debenzylation, analogous S-methyl derivatives remain either unchanged, so that selective debenzylations may be achieved, as in the case of *e.g.* **I** [1, 2];



I

or — sometimes only under more vigorous conditions — a deeper change occurs. *E.g.*, boiling a toluene solution of the S-methyl and 1,S-dimethyl derivatives (**II**; Y = O; R = Me; R' = H, Me) of 5,5-diphenyl-4-thiohydantoin in the presence of aluminum chloride, results in the elimination of the sulfur atom from the molecule together with the methyl group, and a product is obtained which — according to its *molecular formula* — may be regarded as being derived from the initial compound by substitution of the eliminated methylthio group by hydrogen. The same products were formed if we started, instead of the S-methyl-5,5-diphenyl-4-thiohydantoins, either with the corresponding S-benzyl derivatives (**II**; Y = O; R = $PhCH_2$; R' = H, Me) or with 4-thiohydantoins (**III**; Y = O; out of R' and R'' one is H, the other H or Me) unsubstituted at the sulfur atom. It was the investigation of the reaction of this latter type of compounds with aluminum chloride which gave the first hint, together with the data of analysis, about the structure of the reaction products and so about the nature of the reaction. It was namely found that the *same reaction product* is obtained from the reaction of both N-methyl-

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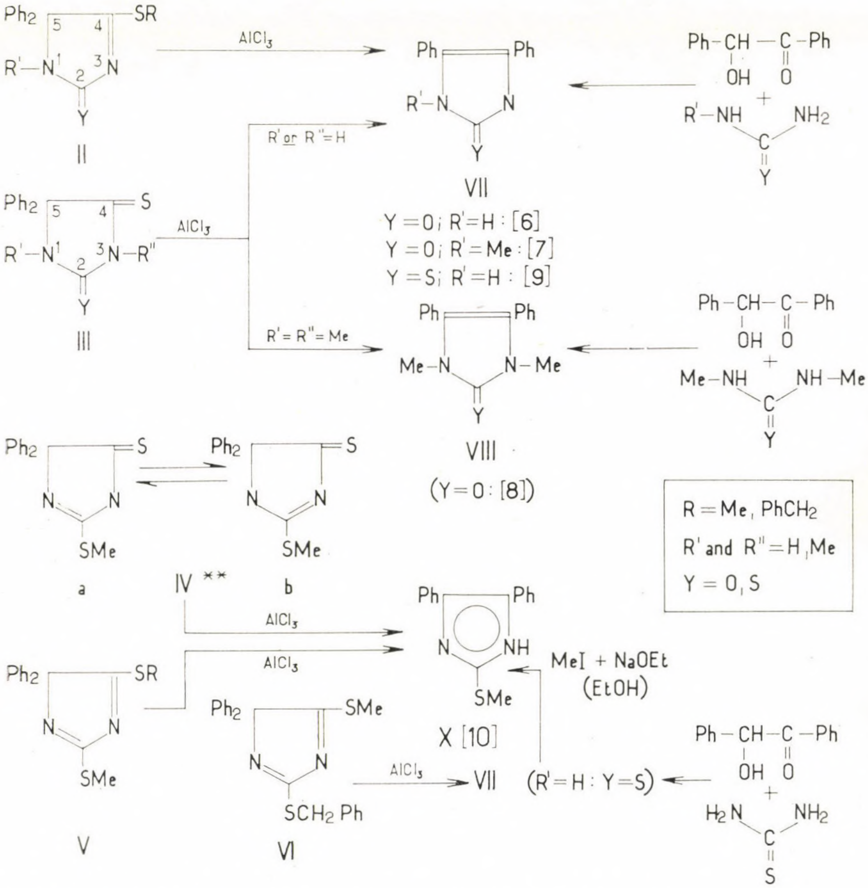
* Part XXIV: Lempert, K., Zauer, K.: Acta Chim. Hung. **50**, 317 (166). — Preliminary Communication see [3].

5,5-diphenyl-4-thiohydantoins (**III**; Y = O; R' = Me and R'' = H; or R' = H and R'' = Me) with aluminum chloride — independently from the fact which of the nitrogen atoms had carried the methyl group. This is only possible if, jointly with the desulfurization, either phenyl migration, or — in the case of one of the N-methyl isomers — methyl migration occurs, too. Unambiguous synthesis of the product (**VII**; Y = O; R' = Me) expected for the first case made it possible to decide in favour of this reaction path [2, 3].

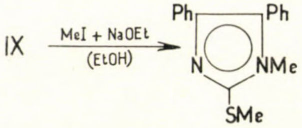
*Scheme 1**



* For the preparation of the starting hydantoin derivatives, see, *e. g.*, [4, 5].
** For the tautomeric equilibrium **IVa** ⇌ **IVb**, see [3].

We then investigated the action of aluminum chloride on 5,5-diphenyl-2-thiohydantoin, 5,5-diphenyl-hydantoin and 5,5-diphenyl-dithiohydantoin, and their N- and S-substituted derivatives; it was found that 5,5-diphenylhydantoin, 5,5-diphenyl-2-thiohydantoin, as well as their S- and N-methyl derivatives failed to react, while in the case of S-benzyl-5,5-diphenyl-2-thiohydantoin, simple S-debenzylation took place [2, 3]. On the other hand, 5,5-diphenyl-dithiohydantoin and its S- and N-substituted derivatives (**II, III**, Y = S; **IV, V** and **VI**) — in accordance with the previously mentioned facts — reacted by rearrangement and elimination of sulfur or mercaptan, respectively (see Scheme 1); desulfurization at C-4 occurs always during the phenyl migration from C-5 to C-4, while the sulfur atom is not cleaved from C-2, and this part of the molecule is only changed in the case of the S-2-benzyl derivative **VI**, where S-debenzylation occurs [2, 3].

In the diphenyl-dithiohydantoin series it was only in the case of the N-methyl derivative of **IVa** when the expected rearrangement product (**X**) could not be isolated. The reason of this — as shown by a separate experiment — was that **X**, prepared unambiguously by another route, gave a tar when acted upon by aluminum chloride.



X

As the methyl derivative of **IVb** is less readily accessible [5], and would also form **X** which is unstable under the conditions of the reaction, the rearrangement of this compound was not even attempted.

During the rearrangement of compounds of type **III** and **IV**, evolution of hydrogen sulfide was observed in all cases. Quantitative determination of the latter showed that 1/2 mole of hydrogen sulfide was liberated from each mole of the starting compound. Based on the hydrogen sulfide evolution the progress of the reaction can be followed and the optimal reaction conditions may be determined.

The optimum amount of aluminum chloride was found to be 2.2 to 2.3 mole; boiled in toluene in the presence of this amount of aluminum chloride, all thiohydantoins furnished the expected 1/2 mole of hydrogen sulfide practically quantitatively within an hour;* in accordance with this, the quantity of the *isolated* rearrangement product was between 80 and 100% of the theoretical amount. Such yields — if the proper reaction conditions stated above are carefully adjusted — may also be obtained in the rearrangement of the S-alkyl derivatives of 4-thio- and dithiohydantoins.

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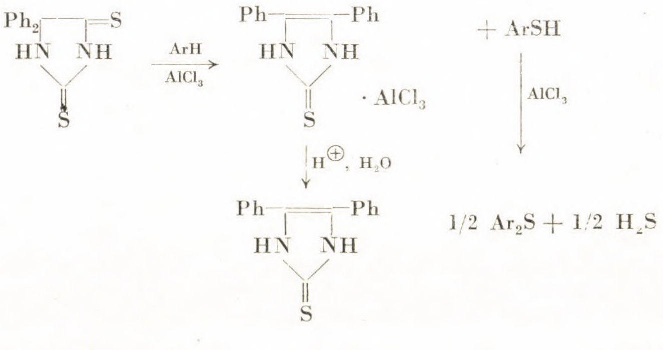
* Small variations in the optimum quantity of aluminum chloride to be used are likely due to the unavoidable inhomogeneity of the reagent.

The fate of the second half of the sulfur cleaved during the rearrangement, which was not liberated as hydrogen sulfide, was investigated, for the time being, in the rearrangement of the starting substance most simple to prepare, *viz.* 5,5-diphenyl-dithiohydantoin. It is known, that diphenylamine can be transformed by *elementary* sulfur, when heated in the presence of aluminum chloride, into phenothiazine, *i.e.*, the sulfur sulfurizes by an S_E mechanism. We presumed that a similar reaction occurred also in our case, so that, at least as a primary product, if benzene was chosen as medium, thiophenol must have been formed. Deuss, on the other hand, showed in 1908 that thiophenols, when warmed in the presence of aluminum chloride in ligroin, are disproportionated to give hydrogen sulfide and an aromatic sulfide [11]. In our case, therefore, we had also to consider the formation of diphenylsulfide, all the more so, since hydrogen sulfide evolution was observed, as mentioned, in all cases during reaction of 5,5-diphenyl-dithiohydantoin and aluminum chloride in toluene as well as in benzene solutions. After decomposition of the crude mixture, obtained by performing the reaction in benzene, by aqueous hydrochloric acid, and removal of the 4,5-diphenyl-4-imidazoline-2-thione produced and of the unchanged thiohydantoin, evaporation of the benzene phase left an oil, in the gas chromatogram of which peaks due to a small amount of thiophenol and to a considerably larger amount of diphenyl sulfide could unambiguously be detected.

When the same reaction was performed in toluene instead of benzene, no peak corresponding to the thiocresols appeared in the gas chromatogram of the oily residue isolated from the reaction mixture in a similar way, but three peaks near to each other appeared in the zone corresponding to the ditolyl sulfides. Comparison with the gas chromatogram of a separately prepared mixture of authentic 2,2'-, 4,4'- and 2,4'-ditolyl sulfides confirmed the identity of these peaks. The peak corresponding to authentic 3,3'-ditolyl sulfide had a different R_F value than the above compounds.

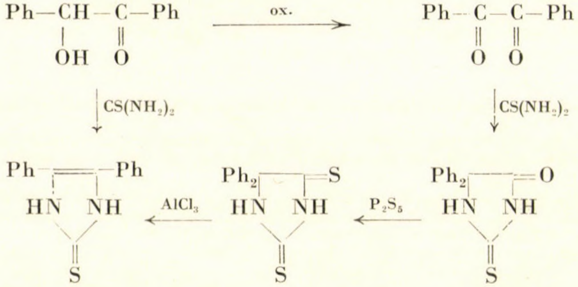
All this indicates that the stoichiometry of our reaction is represented by the following equation:



and, furthermore, that the sulfur atom is cleaved by aluminum chloride in the sextette state. From this, on the other hand, it follows that the phenyl group migrates in all probability cationically. Experiments to prove this point are under way.

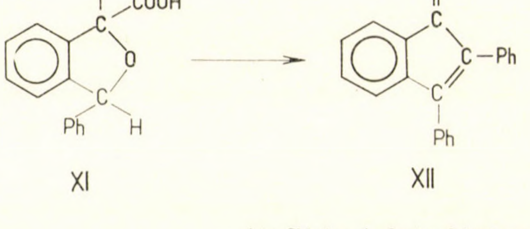
Other experiments by which we want to decide the fate of the cleaved groups and the stoichiometry of the reaction in the case of the S-methyl and S-benzyl derivatives of 4-thio- and dithiohydantoins, are in progress, too.

Scheme 2



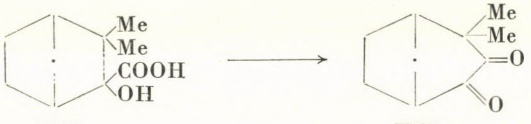
From scheme 2 it is obvious that oxidation and benzilic acid rearrangement, which occur during the reaction series leading from benzoin to 5,5-diphenyl-dithiohydantoin, are, so to say, reversed by aluminum chloride. In this sense, we have to do therefore with a reductive retrobenzilic acid rearrangement. However, while in benzilic acid rearrangement the phenyl group migrates, as commonly known, anionically, the migration of the phenyl group in the course of the rearrangement caused by aluminum chloride is most likely accomplished — as we have seen — cationically.

The literature of retrobenzilic acid rearrangements, known up to now is very scarce. BILTZ and SEYDEL [12] obtained, when heating 5,5-diphenylhydantoin with hydroiodic acid in the presence of red phosphorus, 4,5-diphenyl-4-imidazoline-2-one (**VII**; $R' = H$; $Y = O$) in poor yield among other products. On the other hand, WEISS and BLOCH [13] prepared 2,3-diphenyl-inden-1-one (**XII**) by heating 1,3-diphenyl-pthalane-1-carboxylic acid (**XI**) by itself or with acetic anhydride.



XI XII

It should be noted that both cases represent, similarly to the rearrangement by aluminum chloride in our experiments, *reductive* retrobenzilic acid rearrangement. A retrobenzilic acid rearrangement of non-reductive character was realized by HINTIKKA [14] on camphenilic acid (**XIII**): by heating its lead salt he obtained carbocamphenilon **XIV**.

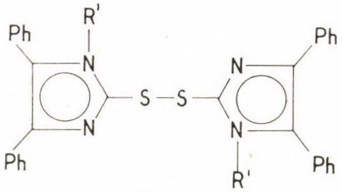


XIII **XIV**

Somewhat more distantly analogous rearrangements are described among the reactions of halogen derivatives of 1,1-diarylethanes and -ethylenes, which may be converted into 1,2-diarylethane and 1,2-diarylacetylene derivatives, respectively (*e.g.*, [15] — [20], [25]). The aryl group, however, seems to migrate anionically in all these cases.

Compounds **VII** are potentially tautomeric systems. Their infrared spectra recorded in KBr pellets, as well as their ultraviolet spectra taken in alcoholic solution are completely analogous to those of compounds **VIII** having fixed structures; this fact shows that they exist both in the crystalline state and in alcoholic solution — at least preponderantly — actually in the form of 4-imidazolin-2-one and -2-thione shown in the formulae.

VII (Y = S; R' = H, Me) is oxidized by mild oxidizing agents, *e.g.* even when recrystallized from dioxane which had been stored for a longer period, to the corresponding disulfide (**XV**).



XV

Experimental*

I. General method for rearrangement of 5,5-diphenyl-thiohydantoins

1 mmole of the 5,5-diphenyl-4-thio- or -dithio-hydantoin derivative in dry toluene (8 ml) was refluxed 1 hr. with freshly sublimed aluminum chloride (2,3 mmole). After cooling, the reaction mixture was poured into 100 ml of aqueous hydrochloric acid (3:1) and stirred for 15 minutes; the precipitated white substance was filtered off, washed with water, dried at 80° and recrystallized from methanol or aqueous methanol. For yields and melting points, see Table I.

Isolation of **VIII**, formed from *1,3-dimethyl-5,5-diphenyl-4-thiohydantoin* (**III**; Y = S; R' = R'' = Me) by aluminum chloride, was carried out, because of its considerable solubility in toluene, in the following manner: after decomposition of the reaction mixture by adding aqueous hydrochloric acid to the toluene solution, further 20 ml of toluene was added. The toluene phase was separated, washed with water until free of acid, and dried over anhydrous

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* All reported melting points are uncorrected.

$MgSO_4$. The solution was filtered, evaporated *in vacuo* and the residue recrystallized from a mixture of benzene and petroleum ether.

Table I

Rearrangement of thiohydantoins with aluminum chloride
(2.3 moles of $AlCl_3$; boiling for 1 hr. in toluene)

Starting 5,5-diphenylhydantoin	Formula	Rearranged product, %	M. p.* C°	Lit.m.p. C°	References
4-Thio-	**III**; Y = O; R' = R'' = H	96.5	320—3	330—5	[6]
S-4-Methyl-4-thio-	**II**; Y = O; R' = H; R=Me	84.0	320—3	330—3	[6]
S-4-Benzyl-4-thio-	**II**; Y = O;R'= H; R = $PhCH_2$—	96.5	320—3	330—5	[6]
1-Methyl-4-thio-	**III**; Y = O; R' = Me; R'' = H	92.0	288—9	289—90	[7]
3-Methyl-4-thio-	**III**; Y = O; R' = H; R'' = Me	99.0	288—9	289—90	[7]
1, S-4-Dimethyl-4-thio-	**II**; Y = O;R' = Me; R = Me	81.5	288—9	289—90	[7]
1,3-Dimethyl-4-thio-	**III**; Y = O; R' = R'' = Me	75.1	183	185	[8]
Dithio-	**III**; Y = S; R' = R'' = H	91.5	318—20	321	[9]
S-4-Methyl-dithio-	**II**, Y = S; R' = H; R = Me	71.5	318—20	321	[9]
S-4-Benzyl-dithio-	**II**; Y = S; R' = H; R = $PhCH_2$-	74.0	318—20	321	[9]
S-2-Benzyl-S-4-methyl-dithio-	**VI**;	99.5	318—20	321	[9]
1-Methyl-dithio-	**III**; Y = S; R' = Me; R'' = H	75.1	283	—	—
3-Methyl-dithio-	**III**; Y = S; R' = H; R'' = Me	84.6	283	—	—
1, S-4-Dimethyl-dithio-	**II**; Y = S; R' = R = Me	78.8	283	—	—
1,3-Dimethyl-dithio-	**III**; Y = S; R' = R'' = Me	66.0	251—2	244—2	[22]
S-2-Methyl-dithio-	**IV**;	94.2	236—7	233—4	[10]
S,S'-Dimethyl-dithio-	**V**; R = Me	71.5	236—7	233—4	[10]
S-2-Methyl-S-4-benzyldithio-	**I**;	71.5	236—7	233—4	[10]

* Uncorrected

II. Synthesis of 5,5-diphenyl-thiohydantoin derivatives

S-Benzyl-5,5-diphenyl-2-thiohydantoin (Cf. [1])

Metallic sodium (0.12 g; 5.0 mg-atom) was dissolved in absolute ethanol (20 ml). 1.18 ml (1.24 g; 10 mmole) of α-toluenethiol and 1.41 g (5 mmole) of S-methyl-5,5 diphenyl-2-thiohydantoin were added. The reaction mixture was refluxed for 8 hrs. During this time the generation of methanethiol practically ceased. Next day the reaction mixture was acidified slightly (pH = 5) by aqueous acetic acid (1:1), the S-benzyl derivative precipitated by water, filtered, washed with aqueous ethanol and dried. Yield: 1.78 g (99.5%), m.p.: 191—2°. Lit. m.p.: 191—4° [21].

S-Benzyl-5,5-diphenyl-4-thiohydantoin (**II**; Y = O; R' = H; R = $PhCH_2$).

(a) 5,5-Diphenyl-4-thiohydantoin (**II**; Y = O; R' = R" = H) (1.30 g; 5.0 mmole) was dissolved in a solution of sodium hydroxide (0.22 g; 5.5 mmole) in 1 ml of water and 8 ml of methanol. Benzyl chloride (0.63 ml; 0.69 g; 5.5 mmole) was added, and the reaction mixture boiled for 5 hrs. Cooling gave a white crystalline precipitate that was filtered off, washed with aqueous ethanol, and dried. Yield: 0.90 g (50.2%), m.p.: 206° (from ethanol).

$C_{22}H_{18}N_2SO$ (358.6). Calcd. N 7.81; S 8.94. Found N 7.91, 7.97; S 8.96, 8.85%.

(b) S-Methyl-5,5-diphenyl-4-thiohydantoin (**II**; Y = O; R' = H; R = Me) (0.70 g; 2.5 mmole) was added to 0.06 g (2.5 mg-atom) of metallic sodium dissolved in the mixture of 10 ml of absolute ethanol and 0.32 ml (0.34 g; 2.7 mmole) of α-toluenethiol. The reaction mixture was boiled for 15 hrs., decolorized by carbon, filtered, and its pH adjusted to 5 by glacial acetic acid. The product was precipitated by water, filtered, washed with aqueous ethanol, and recrystallized from 7 ml of methanol. Yield: 0.23 g (25.8%), m.p. and mixed m.p. with the product obtained under (a) 204—6°.

S-4-Benzyl-5,5-diphenyl-dithiohydantoin (**II**; Y = S; R' = H; R = $PhCH_2$) (*Cf.* [1]).

S-4-Methyl-5,5-diphenyl-dithiohydantoin (**II**; Y = S; R′ = H; R = Me) (1.0 g; 3.36 mmole) was dissolved in a solution of 0.08 g (3.4 mg-atom) of metallic sodium in 30 ml of absolute ethanol and 0.79 ml (0.83 g; 6.7 mmole) of α-toluenethiol. The reaction mixture was refluxed for 7 hrs. until the evolution of methanethiol was completed. After cooling, the reaction mixture was slightly acidified by glacial acetic acid (pH = 5), and the product precipitated by the addition of water. It was filtered off, washed with aqueous ethanol and dried. Yield: 0.95 g (85%), m.p.: 185—6°.

$C_{22}H_{18}N_2S_2$ (374.5). Calcd. C 70.55; H 4.84; N 7.48; S 17.12. Found C 70.85, 70.25; H 5.02, 4.94; N 7.33, 7.16; S 16.92%.

S-2-Methyl-S-4-benzyl-5,5-diphenyl-dithiohydantoin (**I**)

S-4-Benzyl-5,5-diphenyl-dithiohydantoin (**II**; Y = S; R' = H; R = $PhCH_2$) (2.60 g; 7.0 mmole) was dissolved in a solution made of 0.34 g (8.4 mmole) sodium hydroxide, water (2 ml), and methanol (16 ml). 0.523 ml (1.19 g; 8.4 mmole) of methyl iodide was added, and the mixture was allowed to stand for one day. The precipitated white crystalline substance was filtered off, washed with methanol, and dried. Yield: 2.68 g (99%), m.p.: 110—1° (from methanol).

$C_{23}H_{20}N_2S_2$ (388.5). Calcd. C 71.00; H 5.16; S 16.53. Found C 70.75; H 5.29; S 16.50, 16.91%.

S-2-Benzyl-S-4-methyl-5,5-diphenyl-dithiohydantoin (**VI**)

S-4-Methyl-5,5-diphenyl-dithiohydantoin (**II**; Y = S; R' = H; R = Me) (1.20 g; 4.0 mmole) was added to a solution of 0.18 g (4.4 mmole) sodium hydroxide in the mixture of water (1 ml) and methanol (10 ml). Then 0.506 ml (0.56 g; 4.4 mmole) of benzyl chloride was added. The reaction mixture was refluxed for 1 hr. On cooling a yellowish white oil separated which crystallized with difficulty. The white crystalline substance was washed with aqueous methanol and dried. Yield: 1.18 g (76%), m. p.: 87—8° (from methanol).

$C_{23}H_{20}N_2S_2$ (388.5) Calculated N 7.21; S 16.53. Found N 7.20, 7.14; S 16.68, 16.24%.

S-2-Methyl-5,5-diphenyl-dithiohydantoin (IV)

S-2-Methyl-S-4-benzyl-5,5-diphenyl-dithiohydantoin (I) (0.25 g; 0.65 mmole) was refluxed with 0.50 g (3.7 mmole) of freshly sublimed aluminum chloride in benzene for 1 minute. The reaction mixture was cooled, poured into 100 ml of aqueous hydrochloric acid (3:1), and stirred for 20 minutes. The two phases were separated. The aqueous layer was extracted with 15 ml of benzene. The combined benzene solutions were washed with water, extracted twice with 50 ml of 1 N NaOH and washed again with 50 ml of water. The combined aqueous alkaline phases were acidified by glacial acetic acid (pH = 4), the separated product filtered off, washed with water and dried. Yield: 0.18 g (93%), m.p.: 207—8° (from methanol). Lit. m.p.: 211° [4].

III. Unambiguous synthesis of derivatives of 4,5-diphenyl-imidazole and -4-imidazoline

1-Methyl-4,5-diphenyl-4-imidazoline-2-thione (VII; Y = S; R' = Me)*

A carefully pulverized mixture of 5.30 g (25.0 mmole) of benzoin and 2.48 g (27.5 mmole) of N-methyl-thiourea was fused on an oil-bath. Above 190° a vigorous effervescence and generation of vapours commenced; after 1 hr. at 210° the reaction was complete, and the melt solidified. After cooling the substance was ground with 20 ml of ethanol, filtered off, washed with ethanol, and dried. The product was purified by dissolving it in hot 1 N NaOH (1000 ml), followed by filtration; after cooling, the product was liberated from its salt by conc'd HCl. It was filtered off, washed with water until free of acid, and dried. Yield: 5.26 g (79%), m.p.: 283° (from methanol).

$C_{16}H_{14}N_2S$ (266.4). Calcd. C 72.14; H 5.30; N 10.52; S 12.04. Found C 71.92; H 5.06; N 10.37, 10.60; S 12.46%.

1-Methyl-2-methylthio-4,5-diphenyl-imidazole (X)

Metallic sodium (0.12 g; 5.5 mg-atom) was dissolved in absolute ethanol (15 ml) and 1.30 g (5.0 mmole) of 2-methylthio-4,5-diphenyl-imidazole (IX) was added, followed by 0.344 ml (0.78 g; 5.5 mmole) of methyl iodide. Crystallization of the product in the form of white needles started immediately. The reaction mixturewas shortly boiled up until the product dissolved the solution was clarified and filtered. After cooling, the separated crystals were collected by filtration, washed and dried. Yield: 1.03 g (73.6%), m.p.: 121—2° (from aqueous methanol).

$C_{17}H_{16}N_2S$ (280.4). Calcd. C 72.90; H 5.70; N 10.00; S 11.41. Found C 73.07, 72.93; H 5.84, 5.64; N 10.10, 10.03; S 11.16, 11.26%.

Bis-(4,5-diphenyl-2-imidazolyl)-disulfide (XV; R' = H)

(a) 4,5-Diphenyl-4-imidazoline-2-thione (VII; Y = S; R' = H) (0.25 g; 1.0 mmole) was dissolved in hot ethanol (30 ml), and 0.10 g (1.2 mmole) of $NaHCO_3$ was added. Aqueous ethanolic iodine solution (1.0 g of I_2 in 10 ml of ethanol and 2 ml of water) was added dropwise, under vigorous stirring to the hot solution, until the colour of the iodine remained unchanged even after 1 minute of stirring. Excess iodine was removed by $NaHSO_3$, and the solution diluted to 100 ml with water. The separated yellow crystalline substance was filtered off, washed with water, and dried. Yield: 0.17 g (68%), m.p.: 256—8° (from methanol); lit. m.p.: 262° [23].

$C_{30}H_{22}N_4S_2$ (502.6). Calcd. C 71.78; H 4.41; N 11.15; S 12.76. Found C 71.78, 71.99; H 4.46, 4.70; N 11.19, 10.85; S 12.82, 12.90%.

(b) 4,5-Diphenyl-4-imidazoline-2-thione (VII; Y = S; R' = H) (0.10 g; 0.4 mmole) was dissolved in hot dioxane (8 ml) that had *not* been pretreated to remove peroxides. After cooling, the solution was diluted by 20 ml of water, the separated yellow crystalline substance filtered off, washed with water, and dried. Yield: 0.06 g (57.6%), m.p.: 256—8° (from methanol). The product gave no depression of m.p. with the substance prepared according to (a).

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* On the analogy of the preparation of 4,5-diphenyl-4-imidazoline-2-thione by BILTZ and KREBS [9].

Bis-(1-methyl-4,5-diphenyl-2-imidazolyl)-disulfide (**XV**; R' = Me) was prepared similarly, by both methods.

Yield: (a) 70.5%, m.p.: 178° (from aqueous methanol),
(b) 75.5%, m.p.: 178° (from aqueous methanol).

$C_{32}H_{26}N_4S_2$ (530.7). Calcd. C 72.42; H 4.94; N 10.56; S 12.08. Found C 72.17, 72.09; H 4.90, 5.11; N 10.59, 10.38; S 11.95, 12.41%.

IV. Determination of the hydrogen sulfide liberated during rearrangement

The determination of hydrogen sulfide was performed essentially according to BÜRGER and ZIMMERMANN [24]. The reaction mixture under examination (8 ml of anhydrous toluene, 1 mmole of thiohydantoin, variable amounts of $AlCl_3$) was placed into the decomposition flask. From the boiling reaction mixture hydrogen sulfide was swept — in contrast to the original procedure — by a stream of oxygen-free nitrogen into the absorption vessel.

Increasing the quantity of aluminum chloride gradually and keeping the reaction time constant it was found that, when using 2.2—2.3 mmole of $AlCl_3$, practically 0.5 mmole of hydrogen sulfide was generated within 1 hr.; consequently, the reaction was almost quantitative. As shown in Table II, with an insufficient quantity of aluminum chloride little or absolutely no hydrogen sulfide generation was observed, and in such cases the isolated substance was almost pure starting material. (As we had to do with a consecutive reaction, it could have been possible that no or little hydrogen sulfide would evolve, and, nevertheless the rearrangement could have proceeded partly or completely.) In the cases when the calculated quantity of hydrogen sulfide was obtained, the pure rearranged product could be isolated in good yields. In the intermediate cases the product always consisted of a mixture, the *quantitative* separation of which would have caused difficulties; therefore this was not attempted.

Table II

Hydrogen sulfide liberated in the reaction of 5,5-diphenyl-thiohydantoins and aluminum chloride
(reaction time: 1 hr.)

5,5-Diphenyl-hydantoin	$AlCl_3$ (mole/mole of thiohydantoin)	H_2S, in per cent of the theoretical 0.5 mole	Isolated products	M. p. °C	Notes
-dithio-	1.12	—	0.26 g (95.5%)	260—1	starting substance
,,	1.18	40.6			mixture
,,	1.64	54.3			,,
,,	1.94	70.6			,,
,,	2.29	94.6	0.23 g (91.5%)	315—20	rearranged product
,,	2.52	97.5	0.24 g (96%)	318—20	,,
-4-thio-	1.09	5.4	0.25 g (93.5%)	267—8	starting substance
,,	1.28	6.0	0.25 g (93.5%)	267—8	,,
,,	1.57	62.1			mixture
,,	2.02	70.5			,,
,,	2.18	100.0	0.23 g (96.5%)	320—1	rearranged product

V. Gas chromatographic investigations

The gas chromatographic investigations were carried out with a *Carlo Erba Model C* gas chromatograph; a thermal conductivity cell was applied as the detector. The conditions of the determination were as follows:

Column — filling: 20% silicone oil 550/*Celite* 545
length: 2 m
inside diameter: 5 mm
temperature: 200°
carrier-gas — hydrogen
gas velocity about 180 ml/min. (input pressure: 2 kp/cm^2)
evaporator — temperature: 265°
Solid samples were injected in toluene solution.

The authors express their thanks for recording the ultraviolet and infrared spectra to their colleagues dr. László Láng and dr. Pál Sohár, respectively, and for the gas chromatograms to Sándor Békássy. Microanalyses were carried out by the microanalytical staff of the department under the direction of Ilona Balogh-Batta, for which the authors' grateful thanks are due.

SUMMARY

When boiled in an aromatic hydrocarbon with aluminum chloride, 5,5-diphenyl-4-thio- and -dithiohydantoins as well as their N- and S-substituted derivatives suffer retrobenzilic acid rearrangement under the elimination of sulfur or a mercapto group, respectively, to give derivatives of 4,5-diphenyl-imidazole and -imidazoline. In the case of 4-thio- and dithiohydantoins unsubstituted at the sulfur atom, half of the eliminated sulfur is converted into hydrogen sulfide and the other half into diaryl sulfide. This latter product is formed by the electrophilic sulfurization of the aromatic solvent, i.e., the sulfur is eliminated from the thiohydantoin skeleton in sextette state, and so the phenyl group migrates probably cationically.

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1,5-DIKETONES, II

REACTION OF 2-(1-ACETYLPROPYL)-BENZOPHENONES WITH FORMIC ACID

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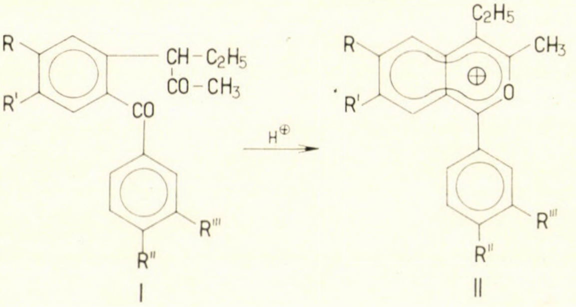
In memoriam Professor A. Müller

Received June 13, 1966

In our preceding paper [1] the transformation of 2-(1-acetylpropyl)-4,3'-dimethoxy-5,4'-diacetoxybenzophenone (**Id**) into isobenzopyrylium formate (**IIa**) by short refluxing with formic acid has been reported. Isobenzopyrylium formates corresponding to other diketones of type **I** could not be obtained in crystalline form.



a : $R = R''' = OCH_3$; $R' = R'' = OH$
b : $R = R' = R'' = R''' = OCH_3$
c : $R = R' = R'' = OCH_3$; $R''' = H$
d : $R' = R''' = OCH_3$; $R = R'' = OCOCH_3$

Refluxing with formic acid for several hours causes profound changes in all diketones of type **I** thus far investigated. *E.g.*, 2-(1-acetylpropyl)-4,5,3',4'-tetramethoxybenzophenone (**Ib**) [10] refluxed with two parts of formic acid for 24 hours gave two yellow crystalline products of different melting points. The IR (Figs. 1 and 2) and UV spectra (Table I) of the lower melting substance, obtained in greater quantity (**VIIb$_1$**) and of the higher melting compound, which is formed in smaller quantity and is more soluble in ethanol, are very similar to each other.

Both ν CO bands of **Ib** have disappeared from the IR spectra and, on the basis of the bands in the region 1600—1500 cm^{-1}, the structure of an isobenzpyrylium salt may also be excluded (*cf.* [2]). On the other hand, the UV spectra proved to be independent of pH and indicated one or more C=C double bonds conjugated with an aromatic ring, since the K-band displayed a great bathochromic shift with respect to veratrol.

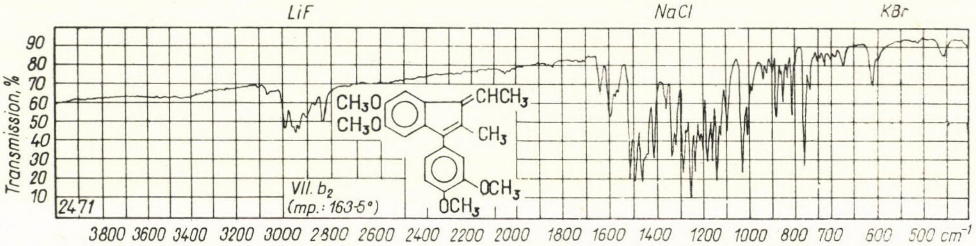


Fig. 1

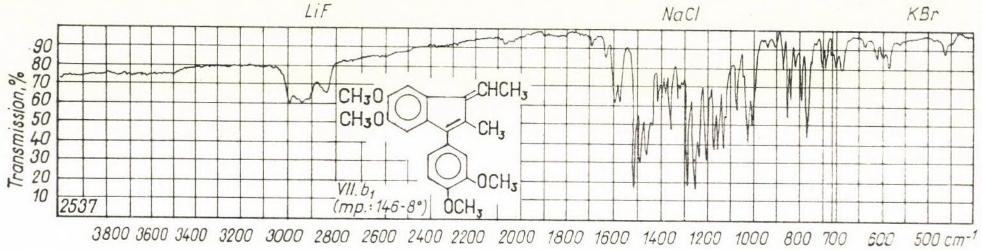


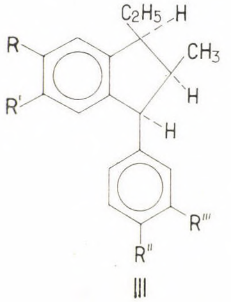
Fig. 2

Table I

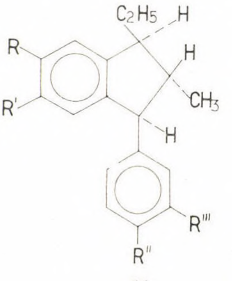
UV spectra of stereoisomeric ethylidene-indenes in ethanol

Compound	λ_{max} (log ε)					
VIIb₁		268 (4.56)	302 (4.07)	315 (4.01)	328 (3.83)	374 (2.91)
VIIb₂		272 (4.54)	303 (4.05)	318 (4.00)	330 (3.84)	365 (3.00)
VIIc₁	225 (4.29)	267 (4.59)		316 (3.97)	340 (3.78)	379 (2.90)
VIIc₂	225 (4.30)	272 (4.57)		317 (3.98)	341 (3.79)	374 (2.85)
VIIa₁		246 (4.46)	302 (4.00)	316 (3.93)	329 (3.75)	393 (2.93)

On catalytic hydrogenation **VIIb₁** as well as **VIIb₂** furnish, by addition of 2 moles of hydrogen, *cis,cis*-diisohomogenol (**IIIb**) [3] while, on reduction with sodium and ethanol, *trans,trans*-diisohomogenol (**IVb**) [3] is obtained.



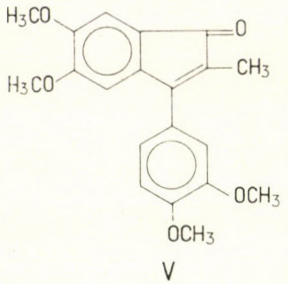
III



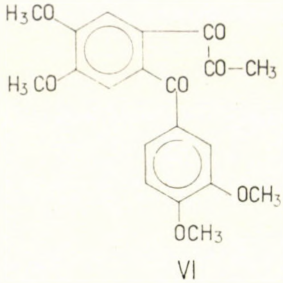
IV

a : $R = R''' = OCH_3$; $R' = R'' = OH$
b : $R = R' = R'' = R''' = OCH_3$
c : $R = R' = R'' = OCH_3$; $R''' = H$
d : $R = R''' = OCH_3$; $R' = R'' = OCOCH_3$
e : $R = R'' = OCH_3$; $R' = OH$; $R''' = H$

Chromic acid oxydation of both compounds **VIIb** yields 2-methyl-3-(3,4-dimethoxy-phenyl)-5,6-dimethoxyindene-1-one (**V**) [4] and 2-pyruvoyl-4,5,3',4'-tetramethoxybenzophenone (**VI**) [4].

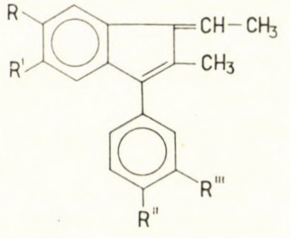


V



VI

According to quantitative elemental analysis and on the basis of the products obtained by oxydation and reduction, compounds **VIIb** are shown to be identical with the two possible cis-trans isomeric 1-ethylidene-2-methyl-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindenes.



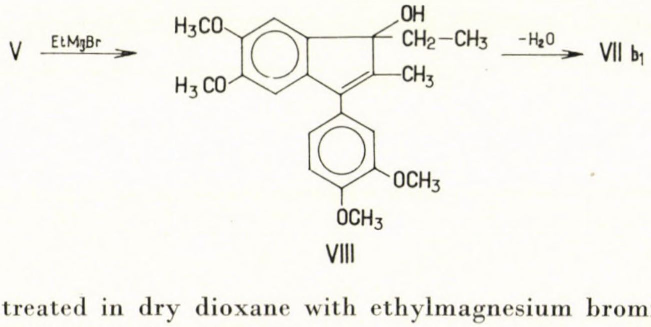
VII

a_1 : $R = R''' = OCH_3$; $R' = R'' = OH$

b_1, b_2 : $R = R' = R'' = R''' = OCH_3$

c_1, c_2 : $R = R' = R'' = OCH_3$; $R''' = H$

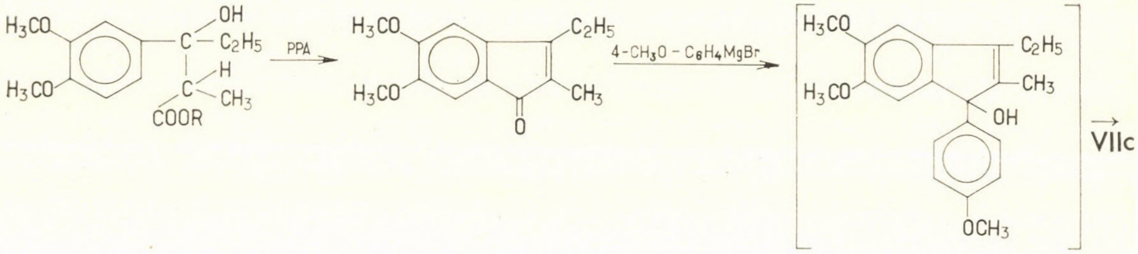
The proposed structures are ascertained also by the following synthesis.



VIII

V was treated in dry dioxane with ethylmagnesium bromide, and the alcohol (**VIII**) obtained dehydrated by potassium hydrogen sulfate or formic acid. The product proved to be identical by m. p., mixed m. p. and spectra with the lower melting stereoisomeride **VIIb**$_1$.

The alternate synthesis starting from **X** and veratrylmagnesium bromide was not even attempted because of the incapability of the latter to take part in Grignard reactions. If, however, **X** was reacted with anisylmagnesium bromide, a yellow substance (**VIIc**$_2$) which, on the basis of its spectra, its elemental analysis and of its reactions, proved to contain the ethylidene-indene skeleton was directly formed by spontaneous dehydration of the intermediate alcohol **XI**.



IX X XI

Isolation of alcohol **XI** primarily formed in the Grignard reaction has been unsuccessfully attempted in several experiments by varying the temperature, the solvent and the ratios of the reactants.

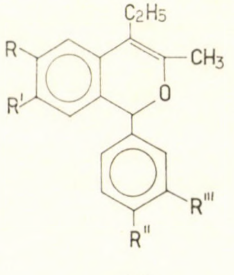
It has been further investigated whether ethylidene-indene (**VIIc**) is formed also by refluxing of the corresponding diketone with formic acid and, if so, whether its steric structure is identical with that of the compound formed in the Grignard reaction. By refluxing **Ic** [5] with twice its weight of formic acid for a period of two hours, a yellow crystalline substance has been obtained which, however, is not identical with the product, **VIIc**$_2$, of the Grignard reaction. Its melting point was found to be lower, its UV and IR spectra, however, to be exceedingly similar to those of **VIIc**$_2$. On catalytic hydrogenation both products furnish, by absorbing two moles of hydrogen, the same colourless saturated compound (**IIIc**); thus **VIIc**$_1$ and **VIIc**$_2$ are stereoisomers.

On the basis of its composition and its mode of formation **IIIc** was thought to be the stereoisomeride of 1-(4-methoxyphenyl)-2-methyl-3-ethyl-5,6-dimethoxyindane (**IVc**) [5], the methylation product of the mixed dimer **IVe** of anethol and isoeugenol. This actually has been proved by chromic acid oxydation of **IIIc** yielding, by cleavage of the five-membered ring, **Ic**, the 1,5-diketone also obtainable on oxydation of **IVc** [5]. (The *trans, trans* structure of the product obtained by mixed dimerization [5] and the *cis,cis* structure of the stereoisomeride formed by catalytic hydrogenation of compound **VIIc**, was in this case, assumed by analogy). Thus, we have had in our hands already the second pair of stereoisomeric ethylidene-indenes, the difference between the members of each corresponding pair surely being due to the different spatial arrangement of the methyl group and the hydrogen atom linked to the double bond of the ethylidene group. An examination of the Stuart models showed that significant additional steric strain existed in neither of the stereoisomerides as compared with the other. Therefore no remarkable differences are found between the UV spectra of the corresponding stereoisomerides and, consequently, their steric structures cannot be established on this basis. Neither was it possible to deduce the steric structure of the stereoisomerides from existing differences in stability.

Information about the relative stabilities of the stereoisomerides could be obtained from their isomerization by acids. On heating with acids, **VIIb$_2$** became completely isomerized into **VIIb$_1$** furnishing thereby an explanation for the observation already mentioned that, on heating with formic acid, **Ib** is chiefly transformed into **VIIb$_1$**. By analogy of the UV spectra, **VIIb$_1$** corresponded to **VIIc$_1$** and **VIIb$_2$** to **VIIc$_2$**, with respect to their steric structure and, therefore, it could be expected that **VIIc$_2$** synthesized by Grignard reaction should be isomerized by acids into **VIIc$_1$**. This, in fact, was found to be the case, again furnishing the explanation for the observation that, from the mixture obtained on heating the diketone **Ic** with formic acid, only **VIIc$_1$** can be isolated.

The third analogous diketone which was reacted with formic acid was **Id.** In our preceding paper it had been reported that this was the first reaction to lead, although in moderate yield, to the formation of an isobenzopyrylium formate (**IIa**)*. More prolonged refluxing with formic acid led both from **Id** and **IIa** to a yellow ethylidene-indene (**VIIa$_1$**) which was transformed by methylation into **VIIb$_1$** described above, and by catalytic hydrogenation into the not yet known *cis,cis*-diisoeugenol (**IIIa**). The latter could be methylated to *cis,cis*-diisohomogenol (**IIIb**) [3].

In addition to the isobenzopyrylium (**IIa**) formate and the ethylidene-indene (**VIIa$_1$**), in this case a third product could also be isolated. The latter is a light yellow crystalline substance and, on the basis of its elemental analysis and IR spectrum, it was identified as 1-(3-methoxy-4-hydroxyphenyl)-3-methyl-4-ethyl-6-methoxy-7-hydroxyisochromene **XIIa**, this being also corroborated by the identity of its methylation product with the isochromene **XIIb** prepared by the LiAlH$_4$ reduction of 1-(3,4-dimethoxyphenyl)-3-methyl-4-ethyl-6,7-dimethoxy-isobenzopyrylium salts (**IIb**) [7].



XII

a : $R' = R'' = OH$; $R = R''' = OCH_3$

b : $R = R' = R'' = R''' = OCH_3$

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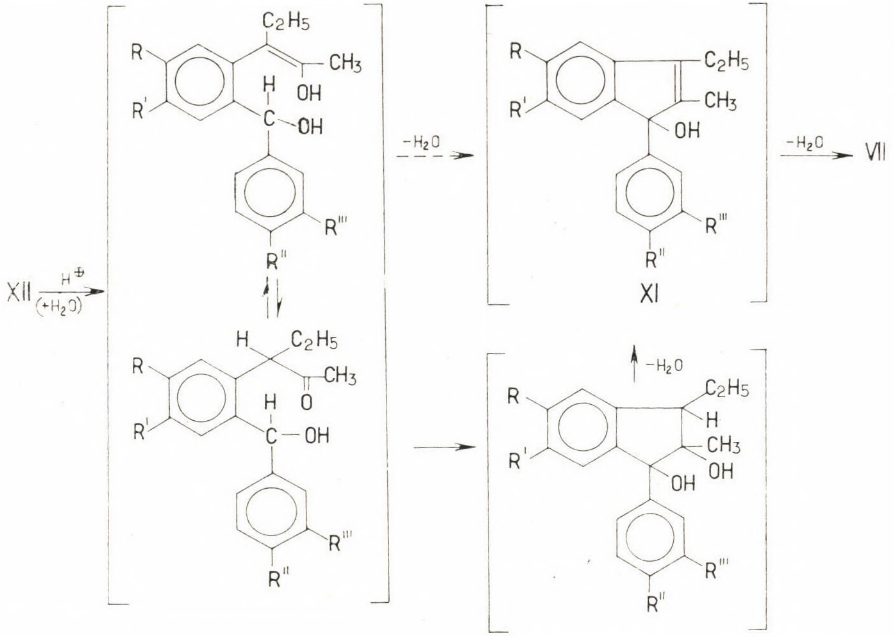
* During salt formation the acetoxy groups of **Id** were cleaved.

On refluxing with formic acid, **XIIa** is transformed into **VIIa$_1$** within 4 hours; therefore, it may be considered as an intermediate of the reaction leading from **Id** to **VIIa$_1$**. Although on refluxing **Ib** with formic acid, in most cases, only the ethylidene-indenes **VIIb** could be isolated, the reaction may be assumed to proceed even in this case through the intermediate isobenzopyrylium (**IIb**) formate and the isochromene **XIIb**. This is evidenced by the facts that under slightly modified reaction conditions **XIIb** could be isolated from the reaction mixture, and that the formation of isobenzopyrylium formates has been demonstrated by spectroscopy [1].

By reason of these results, we assume that the first step of the reaction sequence **I** → **VII** is the formation of an isobenzopyrylium formate (**II**) from the 1,5-diketone (**I**) and formic acid; on prolonged heating this primary product is further converted, just as well as isolated benzopyrylium formates yield ethylidene-indenes when refluxed in formic acid.

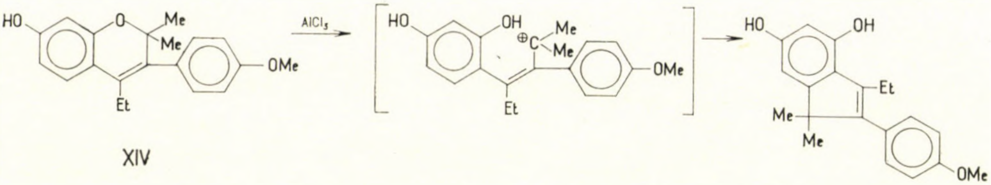
In the following step the isobenzopyrylium salt **II** is assumed to become reduced by formic acid to the isochromene **XII**. Formic acid reductions of nitrogen-heterocyclic compounds, during which only the heterocycle becomes saturated, have been reported several times. Thus, *e.g.* LUKEŠ et al. [8] reacted quaternary salts of pyridine and homologues with formic acid to obtain derivatives of piperidine and Δ^3-piperideine. However, the formic acid reaction of oxygen-heterocyclics, as far as we know, has not been described in literature.



The isochromenes may be transformed into the corresponding ethylidene-indenes in quantitative yield not only by formic acid but also by acetic acid. Accordingly, in this step formic acid does not act as a reducing agent but simply as an acid.*

The next step of the reaction leading to the formation of ethylidene-indenes is assumed to be the fission of the heterocycle of the isochromenes **XII**; this assumption is reasonable considering the enol ether character of these compounds. In the following step cyclization should occur with the elimination of water to give an indenol derivative of type **XI**, the isolation of which was unsuccessfully attempted during the preparation of **VIIc**$_2$ (see above), because it transformed instantaneously into the more stable ethylidene-indene.

A similar transformation, namely the conversion of certain derivatives **(XIV)** of isoflavene into indenes under the action of Lewis acids, was observed by Cook *et al.* [9].



The first step consists, also in this case, in the fission of the heterocycle; however, the closure of the indene ring does not involve the elimination of water but occurs by intramolecular electrophilic substitution.

Experiments to prove the assumed mechanism of the reaction will be continued.

Experimental

Stereoisomeric 1-ethylidene-2-methyl-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindenes (VIIb$_1$ and VIIb$_2$)

15.0 g (39 mmoles) of 2-(1-acetylpropyl)-4,5,3',4'-tetramethoxybenzophenone **(Ib)** [10] were refluxed for 24 hrs. with 30 ml of formic acid. The yellow crystals which separated on cooling were recrystallized from ethanol. Yield: 6.5 g (47.5%) **VIIb**$_1$, m.p.: 146—148°.**

$C_{22}H_{24}O_4$ (352.3). Calcd. C 74.97; H 6.86; O 18.16. Found C 74.77, 75.00; H 6.92, 6.88; O 18.26, 18.26%.

The mother liquor of crude **VIIb**$_1$ was evaporated to dryness and the residue taken up in a small quantity of ethyl acetate. On standing soft yellow needles were deposited. Yield: 0.85 g (6.2%) of **VIIb**$_2$, m.p.: 163—165°.

$C_{22}H_{24}O_4$ (352.3). Calcd. C 74.97; H 6.86; O 18.16; Found C 75.02, 75.03; H 6.75, 6.61; O 18.29%.

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* Treatment of the isochromenes by hydrochloric acid or aluminium chloride gives stable halogen-containing products of unknown structure which cannot be further transformed by treatment with formic acid.

** The synthesis proving the structure of **VIIb**$_1$ is described below.

1-(3,4-Dimethoxyphenyl)-3-methyl-4-ethyl-6,7-dimethoxyisochromene (XIIb)

The above experiment was repeated shortening the reaction time to 4 hours; in this way a 19% yield of a mixture of the above-mentioned stereoisomeric indenes (melting between 133—140° and impossible to separate by a single recrystallization) and a 27% yield of **XIIb**, m.p. 103—105°, were obtained. The latter product was identified by determination of its mixed m.p. with an authentic sample [7], as well as by its IR spectrum.

Reduction of the ethylidene-indenes VIIb

(a) To a boiling solution of 0.5 g (1.4 mmoles) of **VIIb$_1$** in 25 ml of dry ethanol 2 g of metallic sodium was added in small pieces; the solution cleared up within a few minutes. The lemon-yellow solution was evaporated to dryness, the residue taken up in ether and water and, after complete dissolution, the ethereal layer was dried, the solvent evaporated and the residue recrystallized from methanol. Yield: 0.35 g (70%) of trans, trans-diisohomogenol (**IVb**), m.p. and mixed m.p. with an authentic sample [3]: 93—94°. The product was identical with an authentic sample according to its colour reaction with bromine-acetic acid, and its IR spectrum.

(b) The analogous reduction of **VIIb$_2$** with sodium and ethanol also gave **IVb** in 70% yield.

(c) 0.7 g (2 mmoles) of **VIIb$_1$** in 40 ml of dimethylformamide were hydrogenated over palladium-on-charcoal to obtain 0.5 g (72%) cis, cis-diisohomogenol (**IIIb**) [3] as colourless crystals, m.p. and mixed m.p. with an authentic sample: 103—105°. The product was found to be identical with the authentic sample also by its colour reaction with bromine-acetic acid as well as by its IR spectrum.

(d) Catalytic reduction of **VIIb$_2$**, as described above, also gave **IIIb** in 70% yield.

Oxydation of the ethylidene-indenes VIIb

To a boiling solution of 2.0 g (5.7 mmoles) of **VIIb$_1$** in 30 ml of acetic acid a mixture of 4.0 g of chromium trioxide, 20 ml of acetic acid and 1 ml of water was added by drops. After refluxing an hour, the mixture was poured on ice and the precipitate (0.35 g of **V**) recrystallized from acetic acid. Red crystals, m.p. and mixed m.p. with authentic **V** [4]: 188—190°; the IR spectrum was also identical with that of authentic 2-methyl-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyinden-1-one.

By extraction of the first mother liquor of **V** with benzene, 0.65 g of an oily product was obtained which, on repeated recrystallization from methanol, finally melted at 133—134° and, by mixed m.p. and IR spectrum was shown to be identical with authentic 2-pyruvoyl-4,5,3',4'-tetramethoxybenzophenone (**VI**) [4].

Synthesis of the lower melting isomer of 1-ethylidene-2-methyl-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindene (VIIb$_1$)

(a) 0.30 g (0.81 mmoles) of 1-ethyl-2-methyl-3-(3,4-dimethoxyphenyl)-5,6-dimethoxy-inden-1-ol (**VIII**)* dissolved in 2 ml of xylene was refluxed for 3 hrs. with 0.3 g of potassium hydrogen sulfate. After cooling, the mixture was diluted with benzene, washed with water and the residue of the benzene layer recrystallized from ethanol. Yield: 0.24 g (84%) of **VIIb$_1$**, yellow crystals, m.p. and mixed m.p. with the sample prepared from **Ib** (see page 113): 146—148°.

(b) Refluxing 0.3 g of **VIII** for 3 hrs. with 0.6 ml of formic acid yielded the same substance in 85% yield.

2-Methyl-3-ethyl-5,6-dimethoxy-1-indenone (X)

1.0 g (3.0 mmoles) of ethyl 2-methyl-3-hydroxy-3-veratrylvalerate (**IX**) [11] was mixed at room temperature with 10 g of polyphosphoric acid. The honey-like mixture was kept for 40 minutes in a bath of 60—70°, during which period it turned first yellow and finally red,

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* For the synthesis of VIII starting from V, see [13].

and subsequently it was decomposed with ice-water. The yellow pasty product adhering to the walls of the flask was taken up in benzene, the solution washed with aqueous sodium hydrogen carbonate and, after evaporation of the solvent, the residue recrystallized from methanol. Yield: 0.58 g (83%) of colourless crystals, m.p. 135—137°.

$C_{14}H_{16}O_3$ (232.2). Calcd. C 72.23; H 6.94; O 20.66. Found C 72.50, 72,65; H 7.05, 7.18; O 20.41, 20.77%.

Synthesis of the higher melting isomer of 1-ethylidene-2-methyl-3-(4-methoxyphenyl)-5,6-dimethoxyindene (VIIc$_2$)

To a solution of the Grignard reagent prepared from 0.37 g (15 mg-atoms) of magnesium turnings and 2.7 g (15 mmoles) of 4-bromoanisole in 15 ml of dry ether, a solution of 1.0 g (4.3 mmoles) of 2-methyl-3-ethyl-5,6-dimethoxy-1-indenone (**X**) in 10 ml of dry tetrahydrofurane was added under cooling. The resulting green homogeneous solution was refluxed for 5 hrs., poured into ice-water containing ammonium chloride, the aqueous layer extracted with ether, the combined organic layers washed with water, and dried. After the ether and, *in vacuo*, the excess bromoanisole had been removed, the residue was treated with hot methanol; crystallization began either immediately or after short standing. Yield: 1.0 g (72%) of yellow crystals, m.p. 144—146° (from ethyl acetate).

$C_{21}H_{22}O_3$ (322.4). Calcd. C 78.23; H 6.88; O 14.89. Found C 78.64, 78.59; H 7.12, 7.13; O 14.62%. For the UV spectrum see Table I.

Lower melting isomer of 1-ethylidene-2-methyl-3-(4-methoxyphenyl)-5,6-dimethoxyindene (VIIc$_1$)

0.8 g (2.1 mmoles) of 2-(1-acetylpropyl)-4,5,4'-trimethoxybenzophenone (**Ic**) [5] was refluxed for 10 hrs. with 1.5 ml of formic acid. The mixture, irrespective of the precipitate, was evaporated to dryness and the residue recrystallized from ethanol. Yield: 0.35 g (49%), m.p.: 108—109°.

$C_{21}H_{22}O_3$ (322.4). Calcd. C 78.23; H 6.88. Found C 78.36, 78.51; H 7.00, 6.70%.
For the UV spectrum see Table I.

cis,cis-1-(4-Methoxyphenyl)-2-methyl-3-ethyl-5,6-dimethoxy indane (IIIc)

0.5 g (1.5 mmoles) of **VIIc$_1$**, dissolved in 8 ml of dimethylformamide was hydrogenated over palladium-on-charcoal. After the absorption of 2 moles of hydrogen the colour of the solution disappeared. The catalyst was removed, the solution evaporated to dryness and the residue recrystallized from ethanol. Yield: 0.3 g (59%) of colourless crystals, m.p. 88—89°.

$C_{21}H_{26}O_3$ (326.4). Calcd. C 77.27; H 8.02; O 14.71. Found C 77.65; H 7.79; O 14.67%.
Catalytic hydrogenation of **VIIc$_2$** yielded the same product.

Oxidative degradation of IIIc

0.4 g (1.2 mmoles) of **IIIc** was oxidized in 4 ml of acetic acid with 0.3 g of chromium trioxide. After standing overnight, the mixture was poured into water, the aqueous solution extracted with benzene, the benzene solution washed with aqueous sodium hydrogen carbonate and water, dried, and the solvent evaporated. For the purpose of purification, the residue was converted by treatment of its acetic acid solution with a few drops of conc. sulfuric acid into the corresponding isobenzopyrylium (**IIc**) hydrogen sulfate. From the latter the diketone Ic was regenerated by refluxing its aqueous solution for 2 hrs. M.p. and mixed m.p. with an authentic sample [5]: 98—99°.

Isomerization of indenes VIIb$_2$ and VIIc$_2$ into indenes VIIb$_1$ and VIIc$_1$, respectively

(a) Refluxing 0.1 g of **VIIb$_2$** with 2 ml of 5% ethanolic hydrochloric acid for 4 hrs. gave 0.07 g of a substance melting at 138—142° whose IR spectrum was identical with that of **VIIb$_1$**.

(b) **VIIb$_2$** was similarly converted into **VIIb$_1$** by refluxing for 4 hrs. with formic acid.

(c) Under the same conditions **VIIb$_1$** remained unaltered.

(d) Refluxing 01. g of **VIIc$_2$** for 4 hrs. either with formic acid or with ethanolic hydrochloric acid yielded 72 mg of a substance melting at 100—106° whose IR spectrum was identical with that of **VIIc$_1$**.

(e) Under the same conditions **VIIc$_1$** remained unaltered.

Reaction of 2-(1-acetylpropyl)-4,3'-dimethoxy-5,4'-diacetoxybenzophenone (Id) with formic acid

40.0 g (90 mmoles) of **Id** [12] was refluxed for a period of 16 hrs. with 80 ml of formic acid. On cooling 10.0 g (34%) of **VIIa$_1$** separated from the solution, yellow crystals, m.p. 201—202° (from ethyl acetate).

$C_{20}H_{20}O_4$ (324.4). Calcd. C 74.05; H 6.21; CH_3O 19.13. Found C 74.06, 74.10; H 6.27, 6.28; CH_3O 19.30, 19.33%.

The mother liquor of crude **VIIa$_1$** was evaporated to dryness. Refluxing the residue with 100 ml of ethyl acetate gave 7.2 g (20.5%) of 1-(3-methoxy-4-hydroxyphenyl)-3-methyl-4-ethyl-6-methoxy-7-hydroxyisobenzopyrylium (**IIa**) formate [1]; red crystalline plates, m.p.: 153—154°.

After removal of the isobenzopyrylium salt, 4.5 g (14.6%) of 1-(3-methoxy-4-hydroxyphenyl)-3-methyl-4-ethyl-6-methoxy-7-hydroxyisochromene (**XIIa**) separated slowly from the mother liquor on standing, in the form of stout yellow crystals, m.p.: 155—157° (from acetic acid).

$C_{20}H_{22}O_5$ (342.4). Calcd. C 70.15; H 6.48. Found C 69.92, 70.11; H 6.50, 6.56%.

1-(3,4-Dimethoxyphenyl)-3-methyl-4-ethyl-6,7-dimethoxyisochromene (XIIb)

An ethanolic suspension of 0.5 g (1.5 mmoles) of **XIIa** was treated with an ethereal solution of diazomethane whereby it gradually cleared up. After standing overnight, the solution was evaporated to dryness and the residue recrystallized from methanol. 0.35 g (68%) of colourless crystals, m.p.: 103—105°, which were identified with authentic **XIIb** [7] by mixed m.p. and the IR spectrum.

Reaction of IIa formate and of isochromene XIIa with formic acid

(a) 2.0 g (5.2 mmoles) of **IIa** formate was refluxed for 30 hrs. with 4 ml of formic acid; yellow crystals (0.42 g, 25%) were obtained which, by m.p. and mixed m.p. (198—200°) proved to be identical with **VIIa$_1$**.

(b) 0.5 g (1.4 mmoles) of **XIIa** was refluxed for 4 hrs. with 1 ml of formic acid and the yellow crystals which separated on standing were recrystallized from ethyl acetate to yield 0.42 g (90%) of a product, which, by m.p. and mixed m.p. (198—200°) proved to be identical with **VIIa$_1$**.

(c) By treatment with acetic acid instead of formic acid under the conditions described above, **XIIa** was again transformed into **VIIa$_1$**.

Acetylation of VIIa$_1$

A mixture of 0.5 g (1.5 mmoles) of **VIIa$_1$**, 0.2 g of anhydrous sodium acetate and 2 ml of acetic anhydride was heated 1 hr. on a steam bath. After decomposing the excess anhydride by the addition of ice-water, the precipitate was recrystallized from acetic acid to yield 0.45 g (72%) of yellow prisms, m.p. 178—180°.

$C_{24}H_{24}O_6$ (408.4). Calcd. C 70.57; H 5.92. Found C 70.57, 70.39; H 6.20, 6.22%.

Methylation of VIIa$_1$

An ethanolic suspension of **VIIa$_1$** was treated with an ethereal solution of diazomethane. After standing for two days, the resulting clear solution was evaporated to dryness and the residue recrystallized from ethanol. Determination of the m.p. and mixed m.p. (143—146°) with an authentic sample (*cf.* p. 113.), showed the product to be identical with **VIIb$_1$**.

Reduction of VIIa$_1$

1.0 g (3.1 mmoles) of **VIIa$_1$** was dissolved in a mixture of 5 ml of dimethylformamide and 5 ml of acetic acid, and dehydrogenated over palladium-on-charcoal. After the absorption of the required 2 moles of hydrogen the colour of the solution disappeared. The catalyst was removed, the filtrate evaporated to dryness, and the residue recrystallized from methanol to yield 0.5 g (50%) of *cis,cis*-diisoeugenol (**IIIa**), m.p.: 128—130°.

$C_{20}H_{24}O_4$ (328.4). Calcd. C 73.14; H 7.37. Found C 73.04, 73.34; H 7.62, 7.42%.

Acetylation: The residue obtained on evaporating the methanolic mother liquor of **IIIa** to dryness was acetylated with acetic anhydride and sodium acetate to give 0.32 g (25%) of the diacetate (**IIId**) of *cis, cis*-diisoeugenol, m.p. 130—132° (from ethanol).

$C_{24}H_{28}O_6$ (412.5). Calcd. C 69.88; H 6.84. Found C 69.64, 69.99; H 6.82, 7.14%.

Methylation of **IIIa** in alcoholic potassium hydroxide by dimethyl sulfate produced *cis,cis*-diisohomogenol (**IIIb**) [3], m.p. 104—105°.

The microanalyses were made by Mrs. H. Medzihradszky-Schweiger and staff, the spectra were measured and interpreted by Dr. F. Ruff, both at this Institute, to whom thanks of the author are due.

SUMMARY

Prolonged refluxing of hydroxylated and/or alkoxylated 2-(1-acetylpropyl)-benzophenones (**I**) with formic acid gives the corresponding ethylidene-indenes (**VII**). As intermediates isochromenes of type **XII** were isolated in addition to the isobenzopyrylium formates (**II**) obtained also previously. The ethylidene-indenes **VII** exist in pairs of *cis-trans* isomeric modifications; the higher melting and less stable modifications are isomerized by treatment with acids into the corresponding lower melting stable modifications.

While catalytic hydrogenation of the ethylidene-indenes yields the *cis,cis*-modifications (**III**) of the corresponding 1,2,3-trisubstituted indanes, reduction by sodium and ethanol affords the *trans, trans*-modifications (**IV**) of the indanes. By the method described the *cis,cis*-modifications of some dimeric propenyl phenol ethers, thus far unknown, have been synthesized.

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Otto Diels—Walter Ruske

Einführung in die organische Chemie

Die Entwicklung der organischen Chemie ist in mehreren großen Stufen verlaufen; der ständigen Zunahme der experimentellen Erfahrung folgte die Ordnung der Kenntnisse unter allgemeinen Gesichtspunkten. Heute ist für die moderne organische Chemie die intensive Wechselwirkung mit ihren Nachbarwissenschaften charakteristisch. Wechselbeziehung schließt Geben und Nehmen ein. So ist unsere Umwelt in neuerer Zeit durch Kunststoffe, synthetische Fasern, Farbstoffe, Tenside, Pharmazeutika und Insektizide radikal verändert worden. Andererseits haben technische Entwicklungen und neue Aufgabenstellungen Entwicklungen in der Chemie angestoßen oder gefördert. Ebenso vielfältig sind die Wechselbeziehungen zwischen der organischen Chemie und ihren Nachbargebieten in der Quantenchemie, Thermodynamik, Kinetik usw., die ihrerseits die Grundlage für das Verständnis von Reaktionen und Eigenschaften sind.

Entwicklungen dieser Art müssen auch Lehrbücher Rechnung tragen. Sie haben den modernen Entwicklungslinien zu folgen, Einzeltatsachen zusammenzufassen und in abgewogener Dosierung dem angehenden jungen Chemiker zu präsentieren. Unter diesen Gesichtspunkten hat *Walter Ruske* die »Einführung in die organische Chemie«, das bewährte Lehrbuch von *Otto Diels,* völlig überarbeitet und ergänzt. Das Buch bringt dem Anfänger zunächst das grundlegende Tatsachenmaterial der organischen Chemie nahe, zum Teil in einer exemplarischen Behandlung, die durch Hinweise auf die zugehörige Literatur zum Weiterstudium anregt. Es behandelt daneben die Beziehungen zu den modernen Methoden der Strukturaufklärung und führt zum Verständnis der vielfältigen Reaktionsweisen organischer Moleküle. Querverbindungen zur Biochemie, einem immer wichtigeren Gebiet, und zur Medizin werden ebenso behandelt wie Fragen der Technologie.

Eine wesentliche Erweiterung des Umfangs gegenüber dem alten »*Diels*« war nicht zu vermeiden, wollte man nicht das auslassen, was der Leser billigerweise in einer modernen Einführung in die organische Chemie erwarten kann. Die straffe Darstellungsweise und klare Gliederung des »*Diels—Ruske*« wird dem Studierenden jedoch Führung und Hilfe bei seinem Eindringen in das interessante und faszinierende Gebiet der modernen organischen Chemie sein.

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ACTA CHIMICA

ТОМ 51 — ВЫП. 1.

Определение констант стабильности смешанных комплексов типа MA_nB_{N-n}

П. ХУН и М. Т. БЭК

Резюме. Можно различать две различные системы смешанных лигандовых комплексов состава MA_nB_{N-n}: системы, в которых концентрация свободного лиганда является незначительной и системы, в которых эти концентрации соизмеримы с концентрациями комплексов или даже больше последних. Обсуждаются различные методы расчёта констант равновесия. Один из этих методов не требует знания концентрации комплексов, а требует знания соотношения концентраций свободных лигандов при максимальной концентрации каждого смешанного лигандового комплекса.

Сравнительные исследования к построению кривой почернения, с помощью ступенчатого фильтровочного метода

К. ЦИММЕР, Т. ТЁРЁК и Й. БИДЛ

Резюме. Сравниваются результаты, полученные при исследовании нескольких принятых методов кривой почернения. Обсуждаются точки, характеризующие кривую подчернения и приведенную кривую почернения. Описывается метод определения крутости кривой почернения для того случая, когда на снимках спектров имеются лишь такие малые величины почернения, которые соответствуют участку недодержки кривой почернения.

Определялась крутость кривой для спектральных пластинок частично сенсибилизированных также и к видимой области спектра, при различных длинах волн, в случае и спектральных пластинок и фильмов различного типа. Описывается трудность определения крутости в области видимых длин волн, а также странение этой трудности путем применения ступенчатого фильтра, с изменимой постоянной фильтра.

Исследовалась применимость ступенчатых фильтров различного типа, изучалась, далее, зависимость крутости от спектральной линии, от времени проявления и температуры, а также от состава проявителя.

О кинетическом уравнении мономолекулярных гетерогенных каталитичских процессов распада

Г. ШАЙ и П. ТЕТЕНЬИ

Резюме. Авторы исследовали возможность распространения, выведенного и проверенного ранее, кинетического уравнения мономолекулярных гетерогенно-каталитичских реакций на случай, когда поверхностная реакция проходит в две ступени, а также на случай смесей, содержащих два реагирующих компонента. Полученные уравнения имеют форму, аналогичную уравнению, выведенному для более простого случая. Экспериментальные данные, относящиеся и смесям метилциклогексан — циклогексан, подтверждают правильность выведенного уравнения. Результаты однозначно указывают на то,

что первой ступенью дегидрогенизации циклогексана и родственных ему соединений является диссоциационная адсорбция. Затем следует поверхностная реакция — необратимая элиминация и водорода. Скорость распада определяется совокупностью этих двух процессов.

Кинетика и механизм реакций замещения комплексов, IV
Термическое разложение некоторых комплексов типа [Co(x)$_2$амин$_2$]x.

Й. ЖАКО, Ч. ВАРХЕИ и Е. КЕКЕДИ

Было синтезировано более 30 новых, еще неописанных в литературе, комплексов типа [Co(x)$_2$амин$_2$]x (где x — 1,2-циклогександион-диоксим, амин — различные ароматические амины, x —Cl$^-$, Br$^-$, I$^-$, SCN$^-$, ClO$^-$), а также исследовалось их поведение в условиях термогравиметрического анализа. Было установлено, что в случае термического разложения хлоридов, бромидов, иодидов и роданидов образуется стабильный промежуточный продукт типа [Co(X)$_2$амин X]. Анион, находящийся во внешней сфере, замещает одну из молекул амина во внутренней сфере. Из термогравиметрическух данных с помощью метода Хоровиц и Метцгера рассчитывались энергия и энтальпия активации данных реакций замещения. На основе полученных результатов была предложена гипотеза о механизме реакций.

Изотопные эффекты упругости пара, II
Изотопный эффект дейтерия в упругости паров метилового и этилового спиртов

И. КИШ, ДЬ. ЯКЛИ, Г. ЯНЧО и Х. ИЛЛИ

Резюме. В широком интервале температур определялась разница между упругостями паров CH_3OH и CH_3OD, а также C_2H_5OH и C_2H_5OD. И экспериментальных данных, на основе уравнения состояния паров спирта, рассчитывались величины факторов дистилляционного разделения (α). Установлено, что температурная зависимость α хорошо описывается зависимостью Бигелейсена, согласно которой $\ln\alpha = A/T^2 - B/T$ где A и B постоянные величины в одном определенном температурном интервале. Определена величина, так называемой, температуры перемещения, выше которой более тяжелая изотопная модификация является более летучей, по сравнению с более легкой модификацией. Определены также разности между теплотами испарения изотопных соединений.

Электронномикроскопическое исследование золей без изменений в их структуре

И. МАРОТ, Ш. РОРЗЕТЦЕР и Е. РОТБАРТ

Резюме. В сообщении описывается электронномикроскопический препаративный метод и установка для сушки вымораживанием, которая в большой степени удовлетворяет принципиальным и практическим требованиям, предъявляемым к сушке вымораживанием. Установка является простой и легко обслуживаемой, а применяемый метод делает возможным использованием преимуществ микроскопов высокого разрешения.

Исследования были проведены с золями очень чувствительными к коагуляции при замораживании и было установлено, что применение описанного выше метода обеспечивает приготовление препарата без изменений в его структуре.

Влияние неактивных областей поверхности на диффузионный предельный ток вращающегося дискового электрода

Р. ЛАНДСБЕРГ, С. МЮЛЛЕР и Р. ТИЛЕ

Резюме. Обсуждается влияние неактивных областей поверхности на зависимость диффузионного предельного тока дискового электрода от перемешивания. С помощью модельного представления дается общее уравнение зависимости от перемешивания диффузионного предельного тока в случае частично блокированного дискового электрода. Это уравнение количественно согласуется с установленной экспериментально зависимостью диффузионного предельного тока от скорости перемешивания, для восстановления H_2O_2 на парафинированном графите, далее, для окисления манганата и железистого цианида на электродах, содержащих графит. В заключении дается несколько общих замечаний относительно пределов применимости модельного представления для данной проблемы.

Гидантоины, тиогидантоины и гликоциамидины. XXV

Реакция перегруппировки производных тиогидантоина с хлористым алюминием

К. ЛЕМПЕРТ и Й. НИТРАИ

Резюме. При кипячении с хлористым алюминием в ароматических углеводородах 5,5-дифенил-4-тио- и дитиогидантоин, а также их производные замещенные по азоту и сере, переходят в производные 4,5-дифенил-имидазола или -имидазолина при отрыве серы или меркаптана и перегруппировке ретробензиловой кислоты. В случае 4-тио- и дитиогидантоинов, не замещенных по атому серы, одна половина оторвавшейся серы образует сероводорода, другая — диарилсульфид. Последний продукт образуется вследствие электрофильного сульфурирования растворителя, т. е. сера отрывается от гидантоиного скелета в секстетном состоянии и, таким образом, фенильная группа мигрирует, вероятно, катионно.

1,5 дикетоны II

Реакция 2-(1-ацетил-пропил)-бензофенонов с муравьиной кислотой

М. ЛЕМПЕРТ -ШРЕТЕР

Резюме. Гидроксилированные и/или метоксилированные 2-(1-ацетил-пропил)-бензофеноны (I) при продолжительном кипячении с муравьиной кислотой переходят в этилиден-индены (VII). В качестве промежуточных продуктов реакции, кроме изолированных ранее [1] формиатов изобензпирилия (II), были отделены изохромены типа XII. Этилиден-индены (VII) существуют в двух цис-транс изомерных модификациях; плавящиеся при более высоких температурах лабильные модификации изомеризуются, под воздействием кислот, в стабильные модификации, плавящиеся при более низких температурах.

Каталитическое восстановление этилиден-инденов приводит к цис-цис (III) модификации соответствующих 1,2,3-тризамещенных инданов, восстановление же с натриеи и спиртом приводит к транс-транс (IV) модификации этих соединений. Подобным путем удалось получить, неизвестные до сих пор, цис-цис модификации нескольких димерных пропенил-феноловых эфиров.

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SOME PROBLEMS IN THE SEPARATION OF TRACES OF ELEMENTS BY PRECIPITATION II*

MECHANISM OF THE SORPTION OF URANIUM (VI) FROM A CARBONATE MEDIUM

DESORBENT ACTION OF THORIUM HYDROXIDE

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Received November 1, 1965

In our preceding paper we have dealt in detail with the adsorption of uranium(VI) by various adsorbents in a sodium carbonate medium. However, the mechanism of this adsorption was not discussed. In the first part of the present paper we shall treat the problem of mechanism which is not directly mentioned in any of the communications devoted to the adsorption of uranium(VI) from carbonate media.

It has been pointed out by Starik [1] that the formation of the complex $[UO_2(CO_3)_3]^{4-}$ is in fact responsible for the decrease of adsorption by iron(III) hydroxide at pH values over 7. In the opinion of Novikov [2], in turn, the minimum appearing in the curve of sorption plotted against pH values indicates the formation of the carbonate complex proper. Both statements are in accordance with the finding of Markov [3] who proved that in a carbonate solution the maximum amount of the $[UO_2(CO_3)_3]^{4-}$ complex is present at pH 9.0. These references indicate that the desorption is due to the formation of the carbonate complex when the alkaline pH range is attained. However, no analytical evidences are given in the question whether the adsorbed uranium is bound as a carbonate complex or as a UO_2^{2+} ion formed by decomposition of this complex. In order to clarify this problem, the binding of uranium by iron(III) hydroxide in a solution of $Na_4[UO_2(CO_3)_3]$ was investigated.

Preparation of the complex, methods of investigation

Reactive $UO_3 . 2\,H_2O$ was prepared from uranyl nitrate in a photochemical reaction with ethanol, according to Cejka [4]. The product was converted into UO_2CO_3, which on evaporation with sodium carbonate, yielded

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* Part I: Acta Chim. Hung. **50**, 6 (1966).

the desired $Na_4[UO_2(CO_3)_3]$ [5]. The calculated uranium and carbon dioxide contents of the product were 43.91 and 24.35%, respectively, against the values 43.76 and 24.39% found by analysis. Uranium was determined by the Sakharov method [3] while carbon dioxide by the Schulek—Maros method [6]. These methods were employed also in the experiments.

Sorption of uranium(VI) by iron(III) hydroxide in a solution of $Na_4[UO_2(CO_3)_3]$

Since our aim was to establish the ratio only of uranium and carbon dioxide bound by the precipitate, the experimental conditions (such as pH values *etc.*) were not exactly recorded.

In general, our method was as follows. 100 mg of Fe^{3+} was precipitated with ammonium hydroxide, the precipitate separated by filtration, repeatedly washed with boiled-out distilled water, 15 minutes shaken with an almost satured solution of $Na_4[UO_2(CO_3)_3]$, again filtered and washed with distilled water made alkaline with ammonium hydroxide. The content of carbon dioxide and uranium was determined in the precipitate. The results of three parallel determinations are shown in Table I.

Table I

	Uranium, bound mg	CO_2, bound mg	$\frac{CO_2 \text{ equ.}}{U \text{ equ.}}$ bound
1	40.5	1.54	0.20
2	47,5	2.35	0.26
3	40.5	1.65	0.22

Since in the original complex 3 moles of CO_2 fall to one uranium atom, only 6 to 8% of the carbon dioxide, equivalent with the bound uranium can be found on the iron(III) hydroxide. Thus, obviously, the complex is decomposed during adsorption, and practically only the UO_2^{2+} ions are bound. It seems that mechanism of the binding of uranyl ions is not the simple precipitation of the poly- or diuranate, *i.e.* not a strictly taken coprecipitation. According to the assumption of Novikov [2], a coordinative coprecipitation, *i.e.* the formation of hydroxides of mixed nuclei is probable. The linkage may take place by the reaction of the hydroxyl groups, through *ol*-bonds, or eventually by H bonds through H_2O coordinatively bound to iron(III) hydroxide. In the investigation of the sorption of other ions the opinion of Kolarik is very near to this aspect. Namely, Kolarik revived the concept of "sorption complex" applied already earlier by WEISER [8], and operates with reaction equations and even with the stability constants of complexes. According to his data *e.g.* 2 H atoms are exchanged when UO_2^{2+} is bound by manganese dioxide hydrate [7]. Without critically deciding the details of these theories we must note here that their suitability for use is quite apparent, in contrast to the earlier opinions which considered the opposite sign of the ionic charge or of the potential as the prerequisite of any adsorption.

On accepting this mechanism, chemosorption may be taken even as a "copolymerization" of ions or molecules (*e.g.* metal hydroxides) of identical charge.

Binding of uranium by other sorbents in a solution of $Na_4[UO_2(CO_3)_3]$

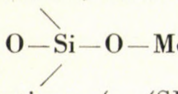
In our further experiments, the binding of uranium from such carbonate complexes was investigated by other sorbents which do not carry any basic hydroxyl groups. The data obtained are presented in Table II.

Table II

Adsorbent	Uranium, bound mg	CO_2, bound mg	$\frac{CO_2 \text{ equ.}}{U \text{ equ.}}$ bound
1 g of silica gel	9	0.34	0.20
1 g of cellulose	12	0.70	0.32
0.1 g of $MnO_2 \cdot n\ H_2O$	13	0.90	0.37

(with 100 ml of $Na_4[UO_2(CO_3)_3]$ solution of a concentration of 1 mg of U/ml, allowed to stand one day)

pH : 8.3

Consequently, only 7 to 13% of the CO_2 amount, equivalent with the uranium, was bound. Thus, also in these cases binding is combined with the decomposition of the complex. On silica gel, binding in ionic form and binding of 0.04 millimoles of uranium can readily be understood (a not insignificant partition ratio when taking into account the relatively high dilution (0.004 *M*) of the solution). According to DESHINA [9], silica gel is, in an alkaline medium, more suitable for binding heavy metal ions, its functional groups  $\diagdown O-Si-O-Me \diagup$ are less stable than the polysilicate formed with multivalent cations $(\equiv (SI-O)_n-Me)$. As regards the binding of ions, the UO_2^{2+} ion occupies a prominent place:

$$Ni^{2+} < Co^{2+} < Cd^{2+} < Zn^{2+} < Ag^{+} < UO_2^{2+} < Cu^{2+}$$

$$Al^{3+} < Mg^{2+} < Fe^{3+}$$

In the case of cellulose as sorbent, binding in cationic form is probably the consequence of the presence of carboxyl groups which prefer an alkaline pH range [10]. Lastly, uranium was bound similarly predominatly in cationic form by manganese dioxide hydrate (prepared according to KOLARIK [11] from a manganese sulfate solution with hydrogen peroxide in a sodium hydroxide medium). The higher rates of binding (over 0.5 millimoles of U/g MnO_2) is not surprising since manganese dioxide hydrate is known to be an excellent adsorbent. According to the observations of several authors [7, 13, 14], this compound is in fact manganese(IV) hydroxide which contains slightly acidic, exchangeable hydrogen ions. On the basis of the investigations of KOLARIK [7], the reaction of UO_2^{2+} and polymeric manganese(IV) hydroxide leads to a bidentate sorption complex characterizable by the formula $UO_2(H_{2-1}A)_2$. The instability constant of this complex is $10^{-3.8}$ (in 1.0 M sodium nitrate).

Some experiments were carried out with the strongly acidic cation exchange resin Varion KS in sodium form. On the basis of our previous experiments, since no excess carbonate is present in the solution, some slight binding of uranium was expected. However, this was not experienced. Quite similarly, no uranium binding was observed by SEREBRYAKOVA [23] with a cation exchange resin at a pH value over 8, in uranium solution containing excess carbonate and in a natural water, either, where uranium was present as a carbonate complex.

Also the uranium adsorption capacity of two samples of active carbon of identical specific surface (800 sq. m. per g) and very different polarity was established, similarly from the solution of the complex. It was found that about two thirds of the uranium amount were bound by the apolar carbon *Nuxit Al—II* while the polar carbon *FL—005* was capable of binding only one fifth of the uranium content. This finding is in contrast to our expectations, up to the present no explanation is available. Since, however, in the analysis of water, the enrichment of uranium by active carbon is suggested by several authors, this problem would be worth of an investigation in detail.

Binding of uranium from a solution of $Na_4[UO_2(CO_3)_3]$ in a column packed with various sorbents

Orientative investigations were carried out with some metal oxides, hydroxides, carbonates and phosphates for the following reasons.

1. To obtain further data in respect to the mechanism of binding.
2. To utilize the results obtained in the explanation of losses occurring in rock analysis.

3. To gather preliminary data for the investigation of the availability of inorganic ion exchangers for analytical or preparative purposes.

In these experiments the adsorbent was packed in an ion exchange column of 1 cm diameter, and the solution of $Na_4[UO_2(CO_3)_3]$ of an uranium content of 1 mg/ml was poured on this column. Hydroxides and phosphates prepared by precipitation were mixed with glass beads previously to packing in the column, thus the usual passing rate of 10 to 20 drops per minute could be maintained. The applied amount of adsorbent and the passed volume of solution was not uniform in that the packing of the column ranged between 0.1 and 40.0 g while the volume of uranium solution between 100 and 500 ml.

The liquid leaving the column was collected in 20 ml fractions which were subjected to determinations of uranium and carbonate. After the completion of each experiment, also the amount of uranium bound by the column was established. In the majority of cases this still did not attain the saturation value because the extension to actual saturation limits would have caused appreciable lengthening of the experimental periods. Still, the obtained results are satisfactory for a qualitative comparison. Accordingly, adsorbents may be classified in three groups:

1. *Adsorbents of high uranium-binding capacity* (over 1 milliequivalent per g of adsorbent)

$$Ca_3(PO_4)_2,\ Zr(HPO_4)_2,\ Ti_3(PO_4)_4,\ Zr(OH)_4,\ Ti(OH)_4,\ Th(OH)_4,\ Fe(OH)_3$$

2. *Adsorbents of a medium uranium-binding capacity* (0.2 to 1.0 milliequivalent per g of adsorbent)

$$Th_3(PO_4)_4,\ MgO,\ ThO_2,\ Al(OH)_3$$

3. *Adsorbents of a slight uranium-binding capacity* (< 0.1 milliequivalent per g of adsorbent)

$$Al_2O_3,\ CaCO_3,\ MgCO_3$$

The following remarks can be made in respect to the results obtained.

1. Also in this case, the binding of uranium was always combined with the decomposition of the complex, even with compounds of decidedly anion exchanger properties, such as $Th(OH)_4$, $Zr(OH)_4$, $Ti(OH)_4$. Apart from the first one or two fractions, the carbonate content of the passing solution was constant. The only exception was thorium hydroxide which is known to bind carbonate ions [14]. Still, the decomposition of the complex appears to be proved even in that case.

2. In most cases, and also with thorium hydroxide, a yellow ring is formed on the top of the column. Also AMPHLETT [16] refers to this fact in case of titanium and zirconium phosphate in a slightly alkaline medium. The ring is certainly a precipitate of uranate whose amount increases with

the volume of liquid passed. Thus, not only the original packing of the column but also the uranate precipitate accumulated on the top of the column act as adsorbents.

3. Uranium bound by the column packing was eluted with 0.1 *M* sodium carbonate, generally with success, excepting, however, calcium phosphate, aluminium hydroxide, titanium hydroxide and thorium hydroxide where the elution is imperfect.

4. It was proved that of the compounds of importance from the aspect of rock analysis, aluminium hydroxide, titanium hydroxide and calcium phosphate may cause essential uranium losses in the case of separation with sodium carbonate. However, it was repeatedly found that no losses occur with calcium or magnesium carbonate.

5. On interpreting the results, the following facts are to be considered. The great extent of uranium binding by zirconium, titanium and thorium phosphates is due to the well-known excellent cation exchange power of these compounds [15, 16, 17]. It is also known from the paper of AMPHLETT [16] that the cation exchange capacity of thorium phosphate is essentially lower than that of zirconium and titanium phosphate. Further, the high uranium-binding capacity of calcium phosphate is already known from mineral-petrographical investigations [18]. The uranium content of sediment rocks is exceeded only by that of carbonaceous formations.

Under the experimental conditions applied (pH 8), the rather basic hydroxides (Th, Zr, Ti) behaved as "zwitter ions", capable of both cation and anion exchange [19]. Since in an alkaline medium they act as good anion exchangers, uranium can readily be eluted from them with a solution of alkali carbonate.

The ion exchange capacity of metal oxides follows from the dissociation of the hydroxide group bound on the surface [20, 21]. For instance in the case of thorium oxide also the existence of a polymeric "zwitter ion" ($Th^+—O^-$) was confirmed.

At last an explanation can be given of the fact that carbonates are least capable of binding uranium. Though calcium carbonate is applied in water analysis for enriching other trace elements [22], uranium is not bound by calcium carbonate to an appreciable extent because the anion of calcium carbonate is just the complexing agent of uranium.

Dependence on pH values of the adsorption of uranium by iron(III) hydroxide in a solution of $Na_4[UO_2(CO_3)_3]$

The results are shown by curve *a* in Fig. 1. The shape of this curve differs from that of the curve obtained in a sodium carbonate medium *(cf.* curve *1a* of Part I). Since no excess carbonate is present in the solution in this case, binding of uranium by iron(III) hydroxide is complete. It can be seen that over pH 12 a part of uranium is dissolved, and this process proceeds up to a nearly complete dissolution. In our earlier paper (Part I) it has been pointed out that this phenomenon takes place at about pH 12.7, with the rise of the hydroxyl ion concentration.

Though in the sorption process the major part of carbonate ions of the uranyl tricarbonate complex are split, and only the uranyl ions are bound, for the sake of comparison the solubility of UO_2CO_3 was investigated in a close pH range. It can be seen in curve *b* of Fig. 1, in the range of pH 8 to 11 the solubilities are very low, and practically constant: about 1 μg U/ml, a value rather fairly in accordance with the data of BLAKE (3 μg/ml) [24] but markedly different from the value of 16 μg/ml given by RAFALSKII [25]

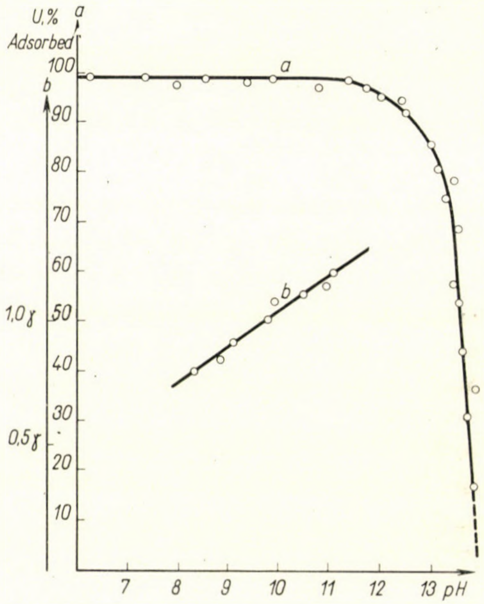


Fig. 1. a) Adsorption of uranium(VI) by iron(III) hydroxide from a solution of $Na_4[UO_2(CO_3)_3]$. 100 mg Fe^{3+} + 100 μg U(VI) coprecipitated with NaOH at 25° in 100 ml volume; *b)* Solubility of UO_2CO_3 in μg/ml, plotted against pH values (pH was adjusted with NaOH)

Though these data doubtlessly refer to the poor solubility of UO_2CO_3, and they prove at the same time that, instead of the poor solubility of uranyl carbonate after the decomposition of the carbonate complex, rather the formation of the sorption complex is responsible for the absence of uranium in the solution (since the solubility of UO_2CO_3 is identical with the initial uranium concentration of the experiment plotted in curve 1*a*).

Desorbent action of thorium in the separation of uranium(VI) in a carbonate medium

In our earlier communications [26, 27, 28] we have already described our experience that in the presence of thorium hydroxide no uranium losses occur in the separation with carbonate, using iron(III) hydroxide, aluminium hydroxide and manganese oxide. This finding was successfully utilized in the analysis of rocks and waters. According to our experiences the desorbent effect manifests itself in rather wide limits of carbonate concentration and temperature, even conditions unfavourable from the aspect of separation. However, besides the practical application also investigations in detail were carried out. Of the results obtained the most characteristic one is that the adsorption of uranium(VI) by iron(III) hydroxide in the presence of thorium hydroxide in a carbonate medium shows a correlation with pH values (curve 2). It can be seen that the desorbent effect is complete in that practically no uranium losses occur in the pH range from 7.7 to 13.0. This means at the same time that also the carbonate concentration can be varied within wide limits without the risk of any uranium losses.

The absence of losses is valid not only for separation carried out in the presence of iron(III) hydroxide.

According to our experiences gathered during several years of analytical practice, no uranium losses occur in silicate and carbonate rocks. It has been described in Part I that in separations conducted with 1.0—0.1 *M* sodium carbonate, uranium losses of 15 to 50% were observed in case of a standard rock sample. When the same rock was separated with carbonate in the presence of thorium, uranium losses ranged only zero to 2% at the same concentrations of sodium carbonate. Separation was similarly good both at room temperature and in hot solutions. However, it is advisable to operate in hot media because the separation is more selective. (The selectivity of separation and its versatile utilization in analysis has been partially discussed earlier [27] and will further be dealt with in a later communication.) According to our investigations carried out thus far, in the cases of samples containing appreciable amounts (1%) of calcium phosphate, uranium losses of 10 to 30% occur even in the presence of thorium when separation is effected with 0.1 *M* sodium carbonate which proved best in serial analysis. Thus, on analyzing phosphate-bearing rocks, 0.5 *M* sodium carbonate concentration is to be employed in order to attain separation without any uranium losses.

Considerations to interpret the desorbent effect of thorium hydroxide

In order to interpret the desorbent effect, investigations were carried out in various directions. A short review of the results is necessary prior to attempt-ing the interpretation of the phenomenon. (Facts already published in previous papers will only be cited here).

1. The desorbent effect is observed not only when hydroxides are previously precipitated (*e.g.* with ammonium hydroxide) and uranium is extracted from the precipitate with sodium carbonate but also when separation with carbonate is carried out directly in the solution itself [27].

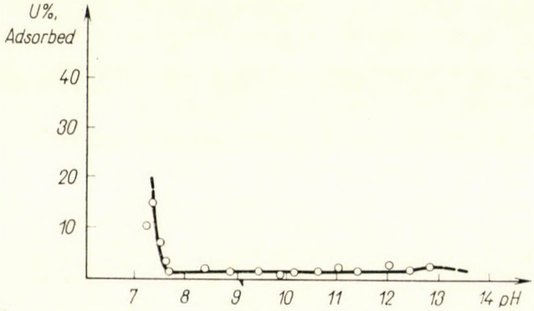


Fig. 2. Adsorption of uranium(VI) by iron(III) hydroxide in carbonate medium, in the presence of thorium hydroxide, plotted against pH values (100 mg Fe^{3+} + 100 μg U(VI) + 20 mg $Th(OH)_4$ coprecipitated with 0.2 *M* Na_2CO_3 at 25° in 100 ml volume)

2. Full desorbent activity is bound to a certain minimum amount of thorium. According to our investigations in the presence of 100 mg of Fe^{3+} 20 mg of Th^{4+} is necessary to attain separation without uranium losses [27]. (This corresponds to 1.8 *M* Fe^{3+} and 0.09 *M* Th^{4+}, *i.e.* in a molar concentration 1/20th part of thorium.)

3. It is apparent from Fig. 2 that the desorbent action manifests itself continuously from pH 7.7 to extremely high values. Thus, in the presence of thorium hydroxide also the maximum appearing at pH 12.7 is absent, due to the hydrolytic decomposition of the uranyl tricarbonate complex.

4. The dissolution of thorium can be controlled within wide limits by varying the carbonate concentration and the temperature. However, the desorbent effect is not limited to the partial dissolution of thorium or to its complete precipitation in that the effect is present in both cases.

5. It was described in Part I of this series [29] that on ageing coprecipitated iron(III) and uranium hydroxide, the extractability of uranium with sodium carbonate markedly deteriorates. When also thorium hydroxide is present in the precipitate, ageing is not decreased and no desorbent effect is observable. When ageing is carried out in a carbonate medium the extractability of uranium is not reduced and, respectively, the amount of coprecipitated uranium does not rise either in the presence or absence of thorium hydroxide.

6. Separation with ammonium carbonate was, in general, not investigated because it is much less selective, and it is more difficult to maintain pH values favourable from an analytical aspect. However, in order to interpret the desorbent effect of thorium it proved to be useful to establish the curve of adsorption against pH values in the presence and absence, respectively, of thorium hydroxide. The experimental results are shown in Fig. 3, indicating that the desorbent effect of thorium hydroxide is quite insignificant. According to our investigations in separations on iron(III) hydroxyde carried out at room temperature in the range of 0.2 to 1.0 *M* ammonium carbonate, uranium losses are throughout high, about 20%, decreasing with the rise of the carbonate concentration at 50—60°. At a concentration of 0.5 *M* ammonium carbonate, uranium losses do not exceed the data attained in separations with sodium carbonate. The results are given in Table III.

Table III

Depedence of the adsorption of uranium(VI) on the concentration of ammonium carbonate
(100 mg of Fe^{3+} and 100 μg of U(VI) precipitated with ammonium carbonate in 100 ml volume· Filtration after allowing to stand an hour.)

Concentration of ammonium carbonate *M*	Uranium losses, %	
	at 25°	at 50—60°
0.05	50	80
0.10	25	27
0.20	22	16
0.30	22	10
0.50	20	6
1.00	20	7

In separations carried out at elevated temperatures, the desorbent effect of thorium hydroxide also begins to act. *E.g.* in a separation with 0.2 *M* ammonium carbonate in the presence of thorium the loss of uranium amounts to only 9% against 16% in the absence of thorium.

7. Also the dependence of uranium losses on the concentration of sodium carbonate at a constant pH value, on iron(III) hydroxide in the presence of thorium hydroxide was investigated. The uranium loss proved to be 25% at 0.01 *M* 13% at 0.03 *M* and 8% at 0.05 *M* both at room temperature and at 80° (the pH value was throughout 10.0) These losses are substantially lower than in the absence of thorium hydroxide. Thus *e.g.* on iron(III) hydroxide alone the loss of uranium was 70% in 0.01 *M* sodium carbonate against 25% in presence of thorium hydroxide.

In the knowledge of results given above our assumption was as follows. Relatively great amounts of CO_3^{2-} ions are bound by thorium hydroxide of excellent anion exchange properties [19]. On the surface of the precipitate the local carbonate concentration increases to such an extent that it is sufficient for preventing the decomposition of the complex ion $[UO_2(CO_3)_3]^{4-}$ and, respectively, it becomes capable of removing the undecomposed ions from the precipitate.

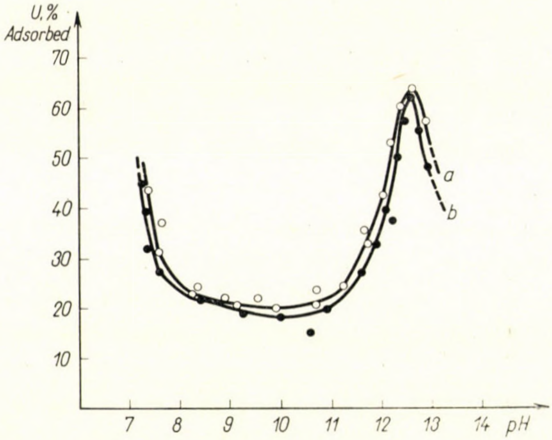


Fig. 3. Adsorption of uranium(VI) by iron(III) hydroxide in an ammonium carbonate medium, plotted against pH values

a) 100 mg Fe^{3+} + 100 μg U(VI) coprecipitated with ammonium carbonate at 25° in 100 ml volume (the pH value adjusted with NaOH); *b)* Same as *a)* but in the presence of 20 mg Th^{4+}

This assumption is in accordance with the fact that in an ammonium carbonate medium at 25° no desorbing effect exists because the concentration of CO_3^{2-} ions is extremely low. At 50—60° the dissociation of ammonium carbonate rises substantially, and also the effect of thorium hydroxide appears.

In our opinion also the results obtained on ageing support thisassumption. Namely, according to the investigations of KOLTHOFF [30, 31], the ageing of metal hydroxides is promoted by hydroxyl ions, and, respectively, the increase of OH^- concentration is combined with the rise of the rate of ageing.

Thus, the adsorption of carbonate ions should decrease on an aged precipitate, and, respectively, a significant ageing cannot take place in a carbonate medium because the number of hydroxyl ions which can be adsorbed by the precipitate is reduced, due to the presence of carbonate ions. As it can be seen in Fig. 2, the desorbent action of thorium hydroxide predominated also in that pH range where on iron(III) hydroxide otherwise the uranium loss increases due to the decomposition of the uranyl tricarbonate complex, and where pH curve shows a maximum.

It can be assumed that this maximum does not appear in the presence of thorium hydroxide because, owing to the binding of carbonate ions by the precipitate, the local OH^- concentration diminishes, and thus uranium is not precipitated any more.

In order decisively to solve the problem, investigations were carried out concerning the carbonate-binding capacity of the various precipitates.

Sorption of carbonate ions by iron(III) hydroxide and thorium hydroxide

The dependence of the sorption on the pH values

To begin with, the extent of binding of carbonate ions was examined on iron(III) hydroxide and thorium hydroxide. At first the amount of carbon dioxide bound immediately after the washing of the precipitate was determined. Later the carbonate content of the filtrate was established by the WARDER method [32], and calculated from the titer decrease of the original sodium carbonate solution. Since this decrease is of relatively small extent, 500 mg of Fe^{3+} and Th^{4+}, respectively, were present in each sample. First precipitates were prepared with sodium hydroxide, then taken up in known amounts of sodium carbonate and of a quantity of sodium hydroxide necessary for adjusting the desired pH value. The results are given in Figs 4 and 5, which conspicuously confirm the correctness of our assumption and even given an explanation for the curve of uranium adsorption plotted against pH values. Carbonate ions are bound to a great extent at pH 11 by iron(III) hydroxide, and at this pH value the adsorption of uranium ranges below 10%. On raising the pH value, the adsorption of CO_3^{2-} gradually diminishes while the uranium loss abruptly increases. However, there is another interpretation of the precipitation of uranium. Also the adsorption of hydroxyl ions by the iron(III) hydroxide precipitate was plotted against pH values *(cf.* curve *c* in Fig. 4), proving that the adsorption of hydroxyl ions increases, as it was expected, with the rise of the pH values. Thus, the surface of the precipitate "becomes alkaline", and the hydrolytic decomposition, and, respectively, the building-up into the precipitate, of the complex $[UO_2(CO_3)_3]^{4-}$ is promoted by the higher local OH^- concentration.

The desorbent action of thorium hydroxide, in turn, can be understood on the basis of Fig. 5. A high carbonate concentration is formed on the surface on the precipitate. This concentration does not diminish with the increase of pH values, and even some rise is experienced at higher pH values. At the same time, the adsorption of OH^- is of a much lower extent, ranging below 1 milliequivalent in the examined pH range. Consequently, the hydroxyl ion sphere

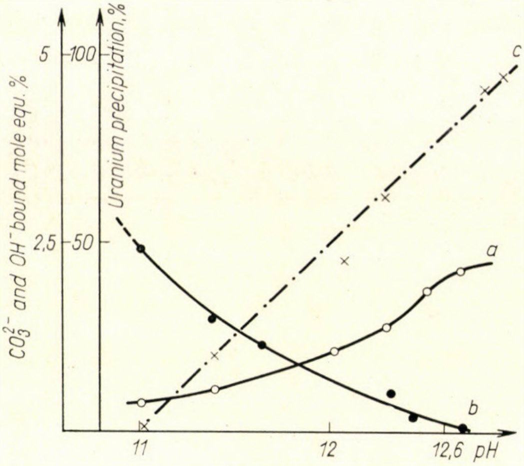


Fig. 4. Binding of carbonate and hydroxyl ions by iron(III) hydroxide, plotted against pH values (500 mg Fe^{3+} precipitated with ammonium hydroxide, then the precipitate washed with 0,05 *M* NaCl until completely free of carbonate. Adjustment of pH was carried out with NaOH, then Na_2CO_3 added to reach a concentration of 0.1 *M*)
a) Uranium adsorption (100 mg Fe^{3+}); *b)* Adsorption of CO_3^{2-} ions; *c)* Binding of OH^- ions

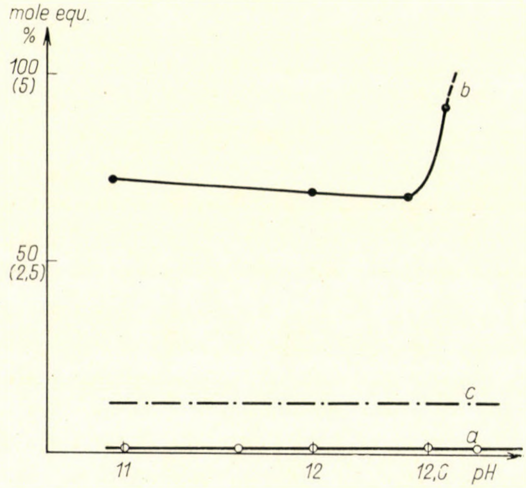


Fig. 5. Binding of carbonate and hydroxyl ions by thorium hydroxide plotted against pH values (conditions of precipitation the same as in Fig. 4. *a)* Adsorption of uranium by a precipitate formed from 100 mg Fe^{3+} + 20 mg Th^{4+}; *b)* Adsorption of CO_3^{2-} ions; *c)* Adsorption of OH^- ions)

promoting the precipitation of uranium cannot be formed on the surface of precipitate.

Also some other experiment were carried out concerning the correlation between the adsorption of uranium and the adsorption of carbonate. Orientative experiments were carried out in order to establish the dependence of carbonate adsorption on concentration. Under identical conditions, iron(III) hydroxide is capable of binding at pH 11, 73 mg of CO_3^{2-} from 0.2 *M* sodium carbonate, 20 mg from 0.1 *M* and less than 10 mg from 0.05 *M* sodium carbonate. Accordingly, the increase of the carbonate concentration is of advantage not only because the stability of the complex in solution is raised but also because the surface of the precipitate is converted to unfavourable for uranium precipitation.

Evidences of the correlation between carbonate adsorption and uranium adsorption were also obtained in other fields. Of these we may mention here the experiment carried out in a medium of 0.21 *M* sodium sulfate, in order to prove that decrease of the binding of CO_3^{2-} ions caused by the concurrence of anions leads to the precipitation of uranium to an increased extent. Purposely a pH value was chosen at which the adsorption of CO_3^{2-} by iron(III) hydroxide is insignificant even in the absence of sodium sulfate, and, respectively, such a low carbonate concentration was chosen at which the desorbent effect of thorium is still slight. The results are presented in Table IV.

Table IV

Effect of sodium sulfate on the adsorption of uranium
(100 mg Fe^{3+}, 50 μg U(VI), 0.01 *M* Na_2CO_3, 11.7 pH in 100 ml volume)

$[Na_2SO_4]$	Th, mg	Uranium adsorption, %
0	0	76—80
0.21	0	80
0	20	52—54
0.21	20	65

It can be seen that at higher salt concentrations also the adsorption of uranium increases.

The results obtained for the carbonate-binding capacity of aged iron(III) and thorium hydroxides is even more conspicuous in that less than 5 mg carbonate are bound by 500 mg of iron(III) hydroxide aged in mother liquor while less than 10 mg by thorium hydroxide aged similarly. As already mentioned earlier, the extractability of uranium with carbonate from aged iron(III) hydroxide is much poorer than from fresh precipitate, and this cannot be affected by adding thorium. Consequently, the real cause is the poorer carbonate-binding capacity of aged precipitates. On the basis of what has been said above it can be taken as proved that the desorbent effect of thorium hydroxide is due to the high carbonate concentration formed on the surface of the precipitate, and, respectively, to the inhibition of a high-extent binding of hydroxyl ions.

Since the pH of precipitation on thorium hydroxide falls between those of iron(III) hydroxide and $UO_2(OH)_2$, we assumed that this is the prerequisite of the desorbent action. In this case the effect would not be observable when the pH precipitation of the carrier precipitate would exceed that of thorium hydroxide. However, in the case of aluminium hydroxide (Fig. 6), the desorbent effect is present though some uranium loss is detectable. At pH 10.4, in turn, the major part of the precipitate is dissolved, though under the experimental conditions applied thorium hydroxide alone could not be dissolved in this way. From this, one may conclude that a mixed hydroxide was precipitated which is connected with the decrease of the active group of aluminium hydroxide, and, respectively, with the eventual desorbent effect of thorium.

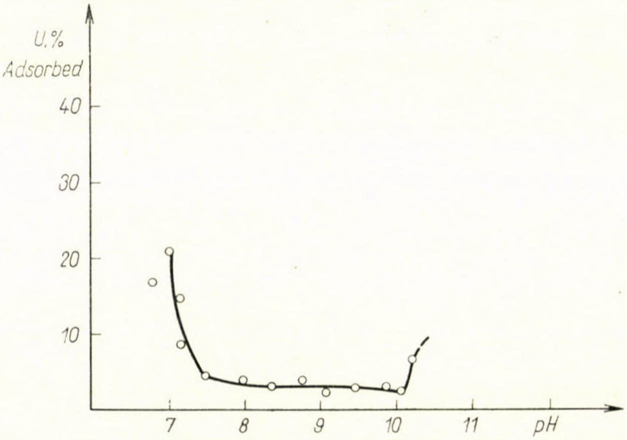


Fig. 6. Desorbent effect of $Th(OH)_4$ on $Al(OH)_3$ precipitate in a Na_2CO_3 medium. 100 mg Fe^{3+} + 20 mg Th^{4+} and 100 μg U(VI) coprecipitated with 0.2 *M* Na_2CO_3 at 25° in 100 ml volume

Investigation of the desorbent effect of other ions

The idea that in addition to thorium also other ions may possess desorbent effects was very plausible. Thus, experiments were carried out with some other ions related to a certain extent, with thorium and with those which are known to form carbonates and partially complex carbonates under certain conditions. In some instances also the carbonate-binding capacity of the examined precipitates was studied. The experimental results are given in Table V.

Table V

Desorbent effect of various ions and carbonate-binding capacity of their hydroxides

Investigation of the desorbent effect: 100 mg Fe^{3+} + 20 mg of desorbent + 100 μg U(VI) with 0.2 *M* Na_2CO_3 in 100 ml volume, stirred 30 minutes at 25°. Investigation of carbonate-binding capacity: the hydroxide precipitate was prepared with sodium hydroxide, and stirred an hour with 0.1 *M* Na_2CO_3

Cation examined	pH value	Uranium loss, %	Amount of cation, mg	pH	CO_3^{2-} bound mg
	at the investigation of the desorbent effect		at the investigation of carbonate-binding		
Zr^{4+}	8.80	6	500	11	36
La^{3+}	9.05	9	500	11	10
Ce^{3+}	9.15	16	500		
Ce^{4+}	8.65	14	500		
	8.80	24	500		
Y^{3+}	9.20	14	100	12.60	10
Be^{2+}	9.0	26	100		
	8.15	21	100		
Zn^{2+}	9.05	50	500	12.25	10
Without any desorbent	8.8—9.15	5			

In the examined pH range the uranium losses with iron(III) hydroxide are lower than in the presence of any other added ion studied. Thus, no desorbent effects could be established, and uranium losses were in the majority of cases definite, while in the case of zinc they were very high. Since however, losses were increased by zirconium and lanthanium only to a slight extent, the curve of uranium adsorption against pH values was established. The results are shown in Fig. 7. The curve discloses a shape differing from that established with iron(III) hydroxide in that the second peak has a more abrupt trend, its value points to complete uranium precipitation, and uranium losses hardly decrease even at high alkalinity values. However, it must be noted that at the pH values belonging to the minimum section of the curve, in the case of rock samples (where uranium losses are essentially higher than with iron(III) hydroxide), zirconium and lanthanium showed certain desorbent effects.

As a supplement and explanation, the results may be completed as follows.

On the basis of the chemical affinities one could have expected some desorbent effect in the case of zirconium, cerium and to certain extent of lanthanum as well. The absence of this effect in case of iron(III) hydroxide may be attributed to the poor carbonate-binding capacity. At the same time, according to our orientative experiments, only a very small number of OH^- ions are bound by zirconium and lanthanum hydroxides (compared to iron(III) hydroxide). This explains why the presence of these ions is of certain advantage from the aspect of uranium losses.

Of the other ions investigated, the strong opposite effect of zinc ions, increasing uranium losses, is very striking. It is probably due to the strong adsorption of hydroxyl ions which used to precede the formation of hydroxo complexes [36], and which suppresses the adsorption of carbonate ions. This presumably plays also a role in the higher uranium losses observed in case of aluminium hydroxide. Thus, the desorbent effect of thorium hydroxide appears to be specific. In optimum cases (iron(III) hydroxide carrier, adequate pH *etc.*) uranium losses are not reduced by zirconium and lanthanum, while in the presence of compounds (mainly of aluminium hydroxide) which adsorb uranium better than iron(III) hydroxide some desorbent effects are perceptible in a tight pH range.

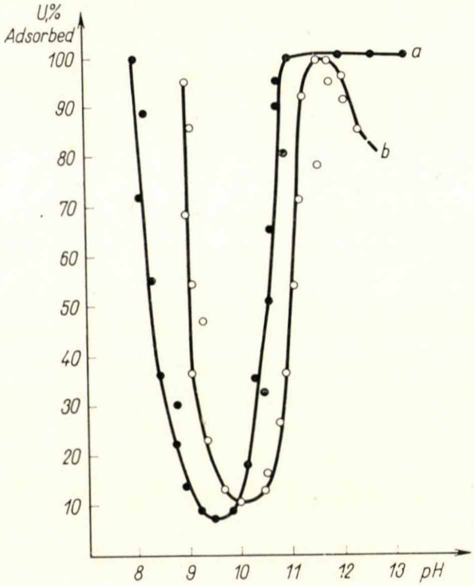


Fig. 7. Effect of $Zr(OH)_4$ and $La(OH)_3$ on the adsorption of uranium (VI) by iron(III) hydroxide in a Na_2CO_3 medium
100 mg Fe^{3+} + 100 μg U(VI); 0.2 *M* Na_2CO_3 at 25° in 100 ml volume
a) 20 mg of Zr^{4+} added; *b)* 20 mg of La^{3+} added

Thanks are due to GY. NAGY for his assistance in the major part of the present experiments.

SUMMARY

In order to clear up the causes of uranium(VI) losses in its separation in carbonate solution, a solution containing $[UO_2(CO_3)_3]^{4-}$ ions was treated with various adsorbents. It was found that uranium losses are due, quite independently of the chemical nature of adsorbents, almost entirely to the decomposition of the complex, and to the binding of UO_2^{2+}- ions. The uranium-binding capacity of some metal oxides, hydroxides and phosphates was investigated, and it was found to range $>$ 1 milliequivalent per g under the applied experimental conditions with hydroxides and phosphates employed as inorganic ion exchangers.

The desorbent effect of thorium hydroxide was examined in detail. It was proved that this effect throughout prevails in the pH range 7.7 to 13.0, and that in the presence of thorium the second peak caused by hydroxyl ions does not appear. The desorbent effect is interpreted by the high carbonate-binding capacity of thorium hydroxide, and, respectively, by its low basicity, which limit the binding of hydroxyl ions.

The dependence on pH values of the adsorption of carbonate and hydroxyl ions was established with iron(III) hydroxide and thorium hydroxide. The results satisfactorily explain the correlation between uranium adsorption and pH values. The increase of uranium adsorption connected with the ageing of the precipitate can similarly be explained by the lack of binding of carbonate ions.

On examining whether other cations (such as Zr^{4+}, La^{3+}, Ce^{3+}, Ce^{4+}, Y^{3+}, Zn^{2+}, Be^{2+}) have desorbent effects, the effect of thorium with iron(III) hydroxide proved to be specific. In rock analysis, adsorption losses are somewhat reduced by the presence of zirconium and lanthanum. This is ascribed to the fact that in the presence of these latter ions, though the carbonate adsorption does not increase, the binding of hydroxyl ions is of a small extent.

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SOME PROBLEMS IN THE SEPARATION OF TRACES OF ELEMENTS BY PRECIPITATION, III

SEPARATION OF SMALL QUANTITIES OF URANIUM(VI) FROM METAL HYDROXIDES BY MEANS OF ALKALI HYDROXIDES

INVESTIGATION OF THE COMPOSITION OF THE URANATE PRECIPITATE

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Sorption of uranium(VI) on $Fe(OH)_3$ in a medium containing NaOH

The sorption of uranium(VI) on metal hydroxides in sodium carbonate media has been reported in a previous paper [1]. On investigating the dependence of sorption on the pH value, it was found that the curve, after passing through a minimum in the pH range between 9 and 11 ascends in dependence on the metal hydroxide used; this range may be narrower, to descend then again from 12.7 pH on. Thus, small quantities of uranium can be desorbed almost completely from $Fe(OH)_3$. It was mentioned that the increase in the loss of uranium above pH 11 is due to the decrease of the stability of the uranium complex $[UO_2(CO_3)_3]^{4-}$ and to the formation of a sorption complex. The decrease in sorption at still higher pH values cannot be ascribed to the regeneration of the carbonate complex, but it must be attributed to the increased hydroxyl ion concentration. In order to clarify this problem, the dependence of the sorption of uranium on the pH value has been measured in NaOH media. (Since pH measurements are inaccurate above the values pH 12, and actually impossible at still higher alkalinity, the sorption values were determined in function of the alkali hydroxide concentration instead of the pH values.)

The results are shown in Fig. 1. (The analyses were carried out by the methods described previously [1].) The carbonate contamination of the alkali hydroxides used for the experiments was negligible. Nevertheless, experiments were also carried out with alkali from which carbonate had been removed with $Ca(OH)_2$ according to Kolthoff. The results were identical.

As it may be seen from curve (*a*), precipitation with NaOH at room temperature is complete up to pH 12, however, the total quantity of uranium is desorbed between pH 12 and 14. This finding may allow the separation of small quantities of uranium from iron. It can be seen from curves (*b*) and (*c*) that the curves become more protracted when KOH or LiOH are used, however, total dissolution occurs at the same alkali concentration.

For comparison, the dependence of uranium adsorption on the alkali concentration was determined also on $Mg(OH)_2$ at room temperature and at 80°C. The results are shown in Fig. 2. It may be seen that the shape of the curves is much flatter than with $Fe(OH)_3$. It is remarkable that the precipitation of uranium is far from quantitative ($\sim 60\%$) at pH 11, while even at an alkalinity above 1 *N* uranium does not pass completely into solution. In all probability, this difference is to be ascribed to the different tendencies for complex formation of Fe^{3+} and Mg^{2+}, and to the lower reactivity of $Mg(OH)_2$. Thus, *e.g.*, the coprecipitation of Ni^{2+} is incomplete on $Mg(OH)_2$ carrier, while it is complete on $Fe(OH)_3$ [8]. Due to its basic properties, $Mg(OH)_2$ does not adsorb alkali [9], showing therefore a tendency to precipitate in the pure state. Moreover, the difference in behaviour may also be due to the fact that at higher alkalinity an uranate compound of magnesium remains adsorbed.

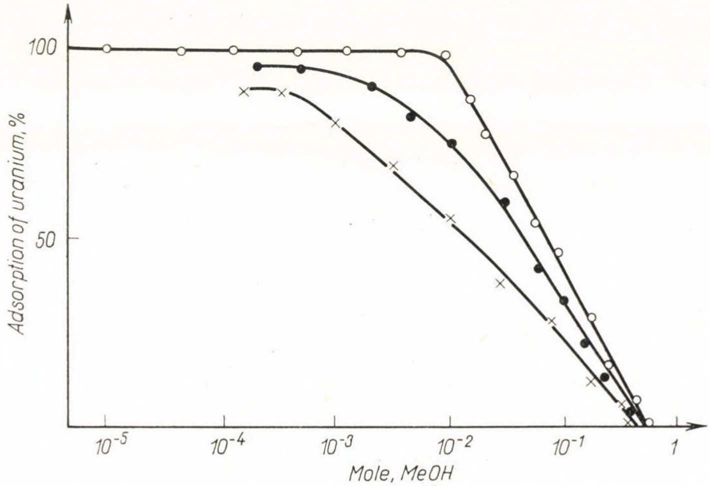

Fig. 1. Sorption of uranium(VI) on $Fe(OH)_3$ in media containing alkali hydroxide [100 mg of Fe^{3+}, 100 μg of U(VI) (precipitated with MeOH), in a volume of 100 ml, filtered after 30 minutes]
(*a*) NaOH; (*b*) KOH; (*c*) LiOH

Our investigations showed that the sorption of uranium is not increased by the presence of calcium. At a corresponding pH (> 13), the presence of 10 to 100 mg of Ca^{2+} per 100 mg of Fe^{3+} does not cause any difference. These results are in agreement with experiences of rock analysis. Thus, according to our observation, after the fusion process with alkali hydroxide, the greater part of uranium remained in the solution when the melt was leached with water. Earlier, we attributed this phenomenon to the carbonate content of the chemicals (KOH, Na_2O_2) used in the fusion process, however, the present results make it obvious that this is not the actual cause. Tests were made with a standard rock sample (B-9), and it was found that after fusion with potassium hydroxide, and after the washing out the precipitate, only 10 to 20% of the uranium was contained in the hydroxide precipitate. This fact makes possible in certain determinations the removal of the greatest part of interfering uranium.

In the same range of alkalinity (pH 11 to 14), also the behaviour of small quantities of thorium was investigated. When 100 μg of Th^{4+} and 100 mg of Fe^{3+} were precipitated with NaOH, it was found that at the most 2% of the thorium gets into the solution. This behaviour may facilitate separation in the determination of the thorium content of uranium ores [10].

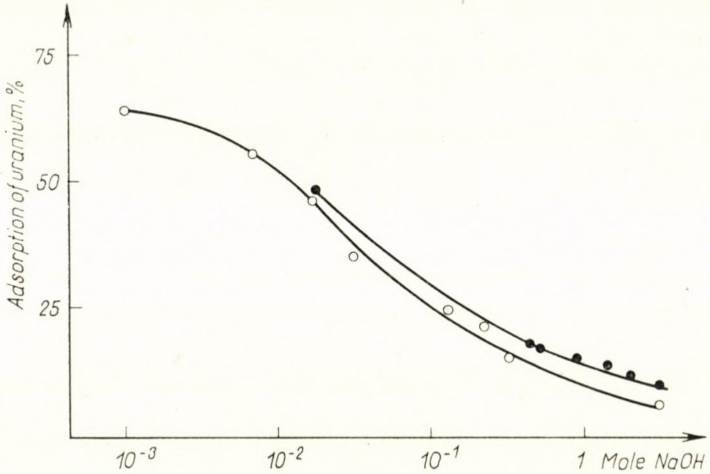

Fig. 2. Sorption of uranium(VI) on $Mg(OH)_2$ in media containing NaOH [100 mg of Mg^{2+}, 100 μg of U(VI), precipitated with NaOH in a volume of 100 ml, filtered after 30 minutes] (*a*) at 25° C; (*b*) at 80° C

Investigations on the mechanism of the dissolution of uranium

Literature references are scarce concerning the dependence of the sorption of uranium upon the pH value in alkaline media. It has been found by STARIK that in the absence of carbonate, precipitation on $Fe(OH)_3$ is complete within the pH range from 3.5—4 to 9 [2], however at pH = 11 sorption decreases to about 80% [3]. STARIK *et al.* are of the opinion that precipitation is due to the opposite charges of $Fe(OH)_3$ and uranium. The curve was recorded only up to pH = 11.

After the publication of our findings discussed above [4, 5], we learned about the work of NOVIKOV [6]. This author studied the precipitation of uranium with potassium hydroxide in the presence of ammonium salts with and without $Fe(OH)_3$ carrier, with uranium quantities from 10 μg to 10 mg. These curves pass through a minimum between pH 9 and 11, which is followed again by an almost complete precipitation of uranium between pH 12 and 13. The final section of the curve shows a descending tendency, with a very steep slope in some of the cases, however, this part falls already in the pH range 14 to 15. NOVIKOV has assumed that the section of the curve presenting the minimum is due to the carbonate of the potassium hydroxide used, while the dissolution at pH values above 12.5 to the formation of the monouranate complex $[Me_2UO_4]$.

On investigating the pH dependence of sorption processes proceeding in alkaline medium on metal hydroxides, the literature reveals that, in general, curves of similar courses [11], have been obtained with anions. This holds true in the cases of molybdenum [12], tungsten [13], chromate, sulphate, phosphate [11], and gallium [14]. At different pH values, but generally up to pH 11, they completely pass into solution.

In view of a certain chemical similarity of uranium to tungsten, molybdenum, and to chromium, the assumption of NOVIKOV, according to which uranium is dissolved in anionic form, *i.e.* as a monouranate, seemed reasonable.

Many publications deal with the alkaline precipitation of macro quantities of uranium and with the investigation of the composition of the precipitates [15—32, *etc.*]. However, the opinions are contradictory concerning the conditions of the formation of mono- and diuranate, and even their existence is debated, so much that literature offers no help in clarifying this problem. The publications either do not support their presented view with experimental data, or incorrect analytical methods are used. A conspicuous example is that though it is well known that the composition of the precipitate is dependent on the pH, some of the authors carry out the analysis on the washed precipitate, after the equilibrium between the precipitate and the solution has been upset just in consequence of the washing.

On the basis of experimental considerations, there is only one simple possibility for the determination of the composition of the precipitate (that is to say the ratio Na : U): the analysis of the solution in equilibrium with the precipitate. By the determination of the quantity of uranium remaining in the solution and by titrating the excess alkali, the ratio of sodium and uranium in precipitate can be calculated. If the possibility of existence of polyuranates of complicated composition (as stoichiometric compounds) is precluded, one may consider the following basic equations:

$$UO_2^{2+} + 2\,HOH \rightarrow UO_2(OH)_2 + 2\,H^+$$

$$2\,H^+ + 2\,OH^- \rightarrow 2\,H_2O$$

Thus, up to the precipitation of uranyl hydroxide two equivalents of alkali are consumed. In the further process, sodium can get into the precipitate only involving the simultaneous disappearance of OH^- from the solution:

$$2\ UO_2(OH)_2 + 2\ NaOH \rightarrow Na_2U_2O_7 + 2\ H_2O$$

$$Na_2U_2O_7 + 2\ NaOH \rightarrow 2\ Na_2UO_7 + H_2O$$

If the non-equivalent adsorption of Na^+ or OH^- plays no part in the process, the ratio Na : U can be directly calculated from the alkali consumption exceeding the two equivalents required for the formation of $UO_2(OH)_2$. (Similarly, KRAUS determined the composition of thorium hydroxide on the basis of the analysis of the filtrate [33]). To ascertain whether the quantity of OH^- consumed for the precipitation is actually equivalent to the sodium getting into the precipitate, in our experiments precipitation was carried out with NaOH containing radioisotope ^{22}Na tracer, and the γ-activity of ^{22}Na in the precipitate was measured. (To eliminate the interference of UX_1 and uranium, the measurements were made at the Na-peak of 0.38 to 0.42 MeV.) Naturally, the precipitate was not washed; after filtering under suction it was weighed, and the quantity of sodium introduced with the small volume (< 1 ml) of solution was taken into correction.

Since these results were in complete agreement with the values obtained by the titration of the hydroxyl ions remaining in the filtrate, the correctness of this analytical method has been substantiated.

Thus, the washing of the precipitate naturally can be avoided, and the equilibrium is not disturbed. By the proper selection of the uranium and the alkali concentrations, the error of analysis can be reduced to a minimum. Since the determination is actually indirect, to reduce the error, expediently the smaller part of the initial alkali concentration is titrated back. This requirement can be better fulfilled in the lower pH range; at higher alkalinity this becomes more difficult, however, generally the weight of the uranium sample was selected so that the difference in 0.1 *N* alkali consumption should not be less than 10 ml in a titration. In our experiments, the weight of uranium was more than 200 mg/100 ml. As it will be seen in the following, at this concentration only a small amount (< 1 mg) of uranium remains in the solution. Owing to this, only an insubstantial correction ($< 0.5\%$) had to be taken when calculating the results.

It is well known that the equilibrium is reached rather slowly. Generally, in our experiments the precipitate was separated after it had been allowed to stand for a day, but informative tests were carried out also with different periods of standing. Since our experiments had the purpose to clarify the mentioned phenomenon of uranium dissolution, particularly the higher pH range was studied in detail. The Na : U ratio has been plotted in function of the pH (Fig. 3). It can be seen that the Na : U ratio in the pH range between 11.8 and 12.9 is 1.00 ± 0.04. This result corresponds to the composition of sodium di-uranate, $Na_2U_2O_7$.

Moreover, from this finding also the conclusion can be drawn that the dissolution of uranium in strong alkaline media cannot be attributed to the formation of monouranate or to some other stoichiometric chemical reaction. (In the absence of a carrier, small quantities of uranium are completely dissolved up to a pH value of 13, though no change in composition is to be detected in this section.)

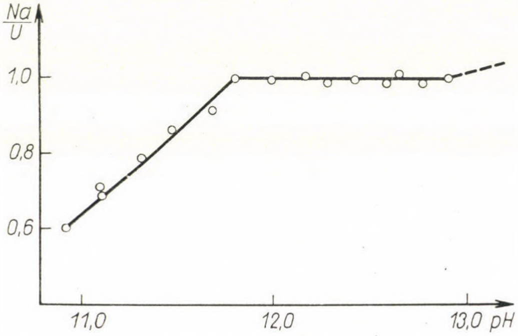

Fig. 3. Dependence of the ratio Na:U on the pH value in the precipitation of uranium(VI) with NaOH [0.0005 to 0.002 *M* $UO_2(NO_3)_2$ precipitated with 20 to 80 ml of 0.1 *N* NaOH at 25° in a volume of 100 ml. Filtered after standing for a day; the filtrate was titrated with 0.1 *N* HCl]. (The pH values above 12 are calculated data.)

The continuous increase of the ratio Na : U below the pH value of 12, shown in Fig. 3, which, within the experimental error, can be considered linear, contradicts the assumed existence of polyuranates of stoichiometric composition [17, 18, 24, *etc.*], while it substantiates the conception of other authors (CHERNAJEV 29, MALY 32, etc.) involving various stages of a gradual transition from uranyl hydroxide to sodium diuranate. The Na : U ratio gradually increases also at the pH values higher than 13, as shown in Fig. 3, but according to informative experiments, even at substantially higher alkalinity (1 *N*) it does not exceed the value of 1.2 or 1.3. It is unlikely that this should indicate a partial uranate formation, and it seems more reasonable to assume a co-precipitation of NaOH. This assumption is substantiated also by three experimental findings. Among these, primarily the fact should be mentioned that the composition of the precipitate changes in solutions containing sodium ions in excess. The results are summarized in Table I.

The Na : U ratio changes also in dependence on the time for which the precipitate is allowed to stand in the mother liquor. Thus, *e.g.*, 2 days of standing at pH 12.8 resulted in the value of 1.05 to 1.09, while 2 weeks in 1.15 to 1.17.

It should be mentioned finally that informative experiments were also carried out concerning the precipitation of uranium with $Ba(OH)_2$ and $Ca(OH)_2$,

Table I

Variation of the ratio Na: U in the sodium diuranate precipitation in dependence on the Na^+ concentration of the solution

(150 mg of U^{6+} precipitated with NaOH in the presence of various amounts of NaCl in a volume of 100 ml at 25° pH = 12.2. Filtration after 16 hours of standing.)

NaCl, *M*	0	0.1	0.2	0.3	0.4
Na : U ratio in the precipitate	1.04	1.16	1.22	1.22	1.25

respectively. For a given pH-value, the alkali : uranium ratio increased in the order Na < Ba < Ca, in agreement with the order of insolubility of the corresponding hydroxides. This renders it very plausible that the precipitate consists of a mixture of diuranate and alkali or alkaline earth metal hydroxide.

Interpretation of the dissolution of uranium

To ensure a correct approach, the dependence of the dissolution of uranium on the uranium concentration was studied. The results are listed in Table II. It is seen that the solubility of uranium is rather high. However, with increasing concentration not only the relative, but also the absolute quantity of uranium remaining in the solution decreases. With uranium quantities higher than 10 mg, where precipitation is instantaneous, the filtrate becomes opalescent during standing, to be followed by coagulation and the separation of additional precipitation. These observations indicate that the dissolution of uranium is a colloid chemical phenomenon. This is substantiated also by the fact that the solubility is decreased in the presence of electrolytes. A few results are shown in Table III.

Table II

The precipitation of uranium(VI) with 0.5 N NaOH
(in a volume of 100 ml, filtration after 30 minutes of standing)

Weight of U sample mg/100 ml	U remaining in the solution mg/100 ml	Weight of U sample mg/100 ml	U remaining in the solution mg/100 ml
1.0	1.0	30.0	26.0
2.0	2.0	40.0	20.0
5.0	5.0	50.0	14.7
10.0	10.0	80.0	7.8
20.0	16.9	100.0	5.7

Table III

The change of the solubility of uranium(VI) in a medium of 0.5 N NaOH in function of the K_2SO_4 concentration

(10 mg of uranium in a volume of 100 ml, filtered after 30 minutes)

$[K_2SO_4]$, M	Dissolved uranium, mg
0.00	10.0
0.05	6.5
0.1	4.5
0.2	2.3
0.5	1.5

Thus, the solubility of uranium in alkaline medium is reduced by increasing electrolyte concentrations. Although the dispersion of the results is considerable (10 to 40%), the trend can be distinctly seen.

As the conditions of precipitation did not vary perceptibly, also the bad reproducibility is to be ascribed to the colloidal nature of the phenomenon.

Just thus great variation of the results was the reason why no reliable values could be obtained for characterizing the change of solubility with the temperature. To prove the colloidal character unequivocally, also electron microscopical photographs were taken of the uranium solution containing sodium hydroxide. One of them is shown in Fig. 4. The pictures confirm that the dissolution of uranium(VI) in alkaline medium is not a simple chemical reaction (formation of uranate), but a colloidal dissolution.

Fig. 4. Electron microscopic photograph of uranium(VI) in NaOH solution
[5 mg of U(VI) dissolved in 100 ml of 0.1 *N* NaOH. The solution was evaporated on a *Formvar* carrier film, and the photograph taken with an electron microscope of Type Tesla BS 242. Accelerator voltage: 60 kV. Magnification: 5000 ×.]

Some possible applications of the separation of uranium(VI) with sodium hydroxide

Rock analysis

It has been mentioned that according to our experiences in rock analysis, after alkaline fusion and subsequent aqueous leaching of the precipitate, the major part of uranium gets into the solution. This increases the permissible uranium content by an order of magnitude in the determination of thorium with arsenazo III, (1,8-dioxi-naphtalene-2,7-bis-[1-azo-1]-2-phenyl-arsonium acid) that is to say, decreases the number of the extraction steps necessary for the separation. Naturally, the utilization of this advantage of alkaline fusion is not restricted to the determination of thorium. This method of separation may be applied in all those cases, where uranium would interfere with the subsequent determination of an element, and this element is retained quantitatively by the hydroxide precipitate carrier in alkaline medium. In our practice up to now, the methods developed for the determination of small quantities of niobium [35] and small quantities of cerium [36] are examples. For the determination of uranium, alkaline separation is less suitable, since the mentioned losses would necessitate a repeated precipitation.

Separation of thorium from uranium for radiochemical purposes

The utilization of this mode of separation for the preparation of uranium-free $UX_1(^{234}Th)$ appeared to be obvious. Our experiments were based on the method of SHCHEKA [34], which seemed to be the most simple and advantageous. This author dissolved 10 g of $UO_2(NO_3)_2 \cdot 6\ H_2O$ in ether saturated with water. In this case, the greater part of UX_1 is contained in the small volume of the aqueous phase. After precipitation on $Fe(OH)_3$ carrier, uranium is removed by repeated washing with $(NH_4)_2CO_3$, and iron, after the addition of thiocyanate, by repeated extraction with ether. According to this procedure, carrier-free UX_1 solution was obtainable with the relatively high yield of 40%, as compared to other methods.

In the method developed by us, the initial extraction with ether though it is one of the main sources of the loss of UX_1, was adopted, since this renders possible to use great initial quantities of $UO_2(NO_3)_2 \cdot 6\ H_2O$.

Our procedure is as follows:

Preparation of UX_1: 10 g of $UO_2(NO_3)_2 \cdot 6\ H_2O$ was dissolved in 30 ml of ether saturated with water. 100 mg of Fe^{3+} and 1—2 g of NH_4Cl were added, to the separated aqueous phase of small volume, and the UX_1 together with the Fe^{3+} carrier were precipitated with NH_4OH. After filtration, the greatest part of uranium was extracted from the precipitate with 25 ml of a 0.1 *M* Na_2CO_3 solution; the precipitate was washed several times with water, and heated for a short time with 100 ml of 1 *N* NaOH. In this way uranium could be removed almost completely. To remove Fe^{3+} (and possible small residual quantities of uranium), the precipitate was dissolved in 25 ml of diluted (1 : 1) hydrochloric acid, and extracted with two 20 ml portions of a 20% tri-*n*-butyl phosphate solution in ligroine. This reduces the uranium content of the solution to $< 0.1\ \mu g/ml$, while the UX_1 yield is about 75%. The highest loss is involved in the separation with ether; the loss of UX_1 in the Na_2CO_3 solution is $< 1\%$, in the NaOH $< 0.1\%$, and in the TBP $< 2\%$.

Finally, another analytical application of the alkaline separation of uranium may be mentioned. In the determination of the ratio $^{234}U/^{238}U$ in natural waters (a value important in radiohydrogeological research), uranium could be separated from traces of UX_1 and from the $Fe(OH)_3$ carried in a solution of pH 13 [5]. The resulting solution is of satisfactory radiochemical purity.

The author is grateful to Mr. GY. NAGY for his cooperation in the experiments. The electronmicroscopic investigations were carried out by Mr. I. GYURKÓ *(Research Department of the Mecseki Szénbányászati Tröszt)*; the author's thanks are due for his help.

SUMMARY

On the basis of earlier investigations (made in connection with the separation of uranium(VI) with carbonate), the behaviour of uranium(VI) in alkali hydroxide medium has been studied in detail. It has been found that small quantities of uranium are quantitatively precipitated on iron(III) hydroxide up to the pH value of 12, to dissolve then gradually when the pH is further increased. The dissolution is quantitative at pH 13—14 if the concentration of uranium is $5 \cdot 10^{-4}\ M$. On increasing the concentration of the electrolyte or with increasing time, the solubility decreases. The composition of the precipitate formed on the addition of NaOH was studied at higher uranium concentrations (0.005—0.02 *M*/lit.) and it has been found that the Na : U ratio of the precipitate is 1.00 ± 0.04 within the pH range between 11.8 and 13.0. This ratio corresponds to the composition $Na_2U_2O_7$, disproving the existence of Na_2UO_4 proposed by several authors for this pH range. In NaCl solutions of higher concentration or after a longer period of standing, the Na : U ratio increases to 1.25. This is possibly due to coprecipitation of NaOH. The high NaOH-(OH^-) adsorption is also substantiated by the fact that the dissolution of uranium is a colloidal process. The latter statement has also been proved by electronmicroscopy.

The dissolution of uranium(VI) in alkaline medium can be utilized both in preparative and in analytical chemistry. So far the method has been applied primarily for the separation from thorium in the determination of the thorium content of uranium ores, as well as for the preparation of UX_1, and for the radiochemical purification of uranium.

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Endre Upor; Pécs, 39-es dandár út 3/a.

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DETERMINATION OF VANADIUM AND NICKEL IN OIL ASH BY SPECTROGRAPHIC ANALYSIS

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The knowledge of the V and Ni content in crude oils and their derivatives gains in importance from the point of view of geochemistry and petroleum genetics, as well as from that of petroleum technology. Determination can be effected directly on petroleum or on the ash of the same. The direct method developed in our laboratory was dealt with in an earlier publication [1]. The development of a method of analysis from ash became necessary partly to increase the sensitivity of the determination, and partly because in some of the cases ash was necessarily the only sample available, boiler ash of fuel-oils.

Preparation of the oil

In case of crude oils, preparation generally involved two steps:

a) Purification of the oil.

b) Preparation of the oil ash (destruction of organic substances).

In the analysis of petroleum derivatives, the first operation can be generally omitted.

Purification of the oil

Crude oil, sampled on the oil field, generally contains various impurities from the soil and water. The proper problem is posed by dehydration, because the oil field brine — often representing up to 20—30 per cent of the sample — can form a very stable emulsion with the oil. Generally, this emulsion can be broken up with laboratory centrifuges of the usual speed of 3000 rpm. Im our laboratory, a centrifuge of a maximum speed of 8000 rpm. was used, permitting the dehydration of most of the samples. Some oils of high asphalt content, in which the density of the heavy components approaches to or just exceeds 1.0, were diluted to 1 : 1 with carbon tetrachloride. Carbon tetrachloride dissolves excellently the oils, reduces their inflammability, and increases substantially the density of the oil-phase. In this case, oil can be separated as the heavier phase. Emulsion breaking agents were not used, because these often contain also the metals to be tested.

Preparation of the oil ash

Several methods are already available for the mineralization of the metals contained in oils [2, 3, 4, 5, 6]. These mostly involve the decomposition or the combustion of the organic matter, but in some of them also extraction is used for the recovery of the metals. Fundamentally, there are three approaches for the decomposition of organic matter, and various methods essentially consist of their combination and improved modifications:

1. Burning of the oil and ignition of the residue.
2. Slow distillation of the oil and ignition of the resuidue.
3. Decomposition of the oil with mineral acids, and ignition of the residue.

Methods 1 and 2 involve the risk of a loss of the metal to be tested during the mineralization process. In method 3 no danger of loss is incurred, however, it has the great disadvantage of being very time-consuming, and therefore it is only seldom used. Various improved forms of method 2 find increasing application. These methods generally attempt to retain with the aid of certain additives the metals to be tested without loss in the ash. McCoy describes for example an ashing technique [2], which combines the relative speed of dry distillation with the reliability of wet decomposition. Referred to 100 g of the oil, 10—20 drops of concentrated sulphuric acid are added to the sample to be tested. According to McCoy, this small amount of mineral acid is sufficient to retain quantitatively V and Ni. Since this technique is relatively simple and rapid, we decided to check experimentally, whether any loss of metal occurs. Two experimental oils were analysed by four different methods;

a) With a quenched electrode [1].
b) By slow distillation.
c) By slow distillation, adding 20 drops of conc. H_2SO_4/100 g of oil to the sample.
d) By wet decomposition.

In the case of V, no loss was found, all four methods giving within limits of experimental error the same result. The analysis of Ni gave by about 10—12 per cent lower values for the sample, that was ashed by slow distillation in absence of sulphuric acid, while the other three methods yielded, within experimental error, identical results. Thus, it was verified that decomposition by slow atmospheric distillation actually causes, primarily for Ni, a negative error, while decomposition by distillation in the presence of sulphuric acid was proved to be equivalent with wet decomposition, yielding correct analysis results.

Procedure for the preparation of the ash

Weigh about 200 g of pure crude into a transparent quartz dish, and cautiously heat over a gas flame until the oil becomes high-fluid. Next, add drop by drop 40 drops of concentrated H_2SO_4, mix thoroughly with a glass rod, clean the rod with a filter paper and throw this paper into the sample. Heat the oil, and take care that its temperature always remains just below the flash point. Carry out this operation under a hood, until a tarry carbonized residue is obtained. Place the dish into a muffe furnace ,and ignite the sample at 550°C until the complete disappearance of carbon traces.

For oils having very low ash and metal content, the procedure is repeated several times, or alternatively, light fractions are previously distilled of from a larger oil sample (after adding the prescribed quantity of conc. H_2SO_4), and only the residue of this distillation is subjected to the described ashing procedure.

Preparation of the ash for spectrography

Determinations from oil ash, primarily that of V, were undertaken by several authors, and some of the data published in literature were investigated by us in detail [3, 4, 5, 6]. The powder preparation technique in two descriptions appeared to suit particularly our laboratory conditions. **Anderson** and **Hughes** [3] admix the oil ash in a proportion of 1 : 3 with SiO_2 powder containing 1 per cent of Ti, and subsequently this mixture in a proportion of 1 : 2 with graphite powder of spectral purity. This final mixture is excited, Ti serving as internal standard. Synthetic standards are used, which are prepared by the admixture of suitable concentrations of the pure metal salt with NaCl or NaCl—CaO powder, and preparing this mixture as described above. This method was adapted also by **Kanehan** [6] with some modifications, involving the admixture of the ash in a proportion of 1 : 9 with the buffer, and the mixing of the metal salt with graphite powder in the preparation of the standards.

Our own experiments, undertaken for the checking of these methods, showed that the ash becomes excessively diluted by buffering in a proportion of 1 : 9, causing a substantial decrease in sensitivity, and particularly in that of V. When buffering in a proportion of 1 : 3, sensitivity seemed to be satisfactory. Moreover, it was found that Ti cannot be used as internal standard, because some of the ashes of the Hungarian oils contain considerable quantities of Ti. The same holds true for Cr, the applicability of which has also been tested. On the basis of these experiments, we decided on the use of Co as internal standard. Although oil ashes often contain a small quantity of Co accompanying Ni, and generally in a proportional amount to the quantity of the latter, Co-lines are already undetectable on the photos of the spectrographic powder mixtures. Synthetic standards were prepared according to ANDERSON and HUGHES with NaCl.

In the preparation of spectrographic powder mixtures, the homogenization of the various powders is of paramount importance. Concerning the duration of this homogenization, opinions in literature are different. Some of the authors are even of the opinion that a suitable homogenity can be attained only by rubbing, for several hours in an agate mortar. The required homogenization time was investigated experimentally. Systematic errors were calculated for tests on samples homogenized in an agate mortar for 5, 10, 20 and 40 minutes, respectively. These experiments were repeated several times, and always gave the remarkable result that samples homogenized for 5 minutes gave the most accurate analyses and that an increase of the time of homogenization gives more deviating results. Presumably, this may be explained by an increase in the degree of dispersion with rubbing time, influencing to a certain degree also the conditions of evaporation, and moreover, air turbulences formed on discharge mobilize easier the non excited substance, disturbing hereby the uniformity of the discharge. It should be mentioned that the average error of the samples homogenized for 5 minutes was but 2.5 to 3.5 relative per cents. This can be considered as rather satisfactory in the excitation of powder mixtures. Thus, it was established that a homogenization of the powder mixtures longer than 5 minutes is not only unnecessary but actually harmful. However, it is possible that this finding is not valid for powder mixtures of a different composition.

Procedure for the preparation of the powder mixture

Weigh on a torsion balance 30 mg of oil ash, 90 mg of SiO_2, to which previously Co-salt has been mixed in a quantity so as to give 1 per cent Co content, and 240 mg of graphite powder into an agate mortar. Rub the mixture intensively for 5 minutes, and store it until use in a glass vial. Excitation is effected in the bore of a graphite electrode with low voltage alternating current arc.

Analysis and reference lines

In the selection of the analysis lines, we departed from the works of ANDERSON and HUGHES, and of KANEHAN, since the line V 2977.5 recommended by these authors is unsuitable for the measurement of low concentrations. Ni was not determined by these authors, and they used Ti instead of Co as internal standard. Our aim was to develop a uniform method for all natural oil ashes, and this stipulated for both metals a measuring range from 0.005 to 30 per cent. Obviously, this great interval of concentration could not be handled by one pair of lines for both metals. Many experiments had to be carried out until for both metals those pairs of analysis lines were found which met all the requirements.

Vanadium

The lowest concentrations can be measured only by the aid of V 3185.4, one of the most sensitive atom lines. When using background correction, the lowest measurable concentration was 0.005 per cent. However, this line has a high tendency for self-absorption, and thus, could not be used above a V-content of maximum 0.5 to 0.6 per cent.

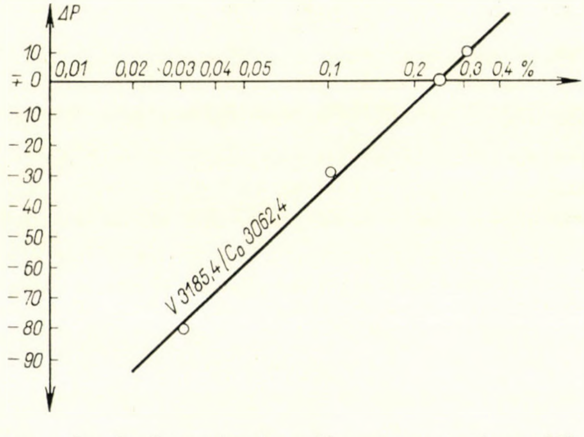

Fig. 1. Calibration curve for the determination of low concentrations of V. Measuring range: 0.005—0.6 per cent

For the measurement of higher concentrations, the ion line V 3110.7 was used. This line can already be measured at concentrations of a few tenth per cent, and gives up to 10.0 per cent an excellent calibration line. However, above this concentrations, this line becomes unusable due to self-absorption, too. Generally speaking, in the whole spectrum only a single atom line, V 2722.6, could be found, which did not show self-absorption even at a concentration of 30 per cent, and met also other measuring requirements.

With the first two selected lines the atom line Co 3062.2, with the third selected line the atom line Co 2650.2 was used as reference line.

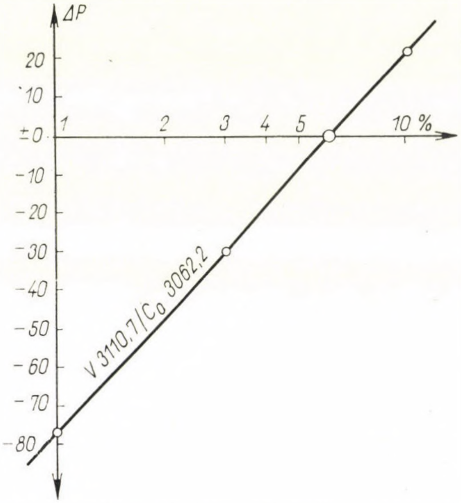

Fig. 2. Calibration curve for the determination of medium concentrations of V. Measuring range: 0.6—10.0 per cent

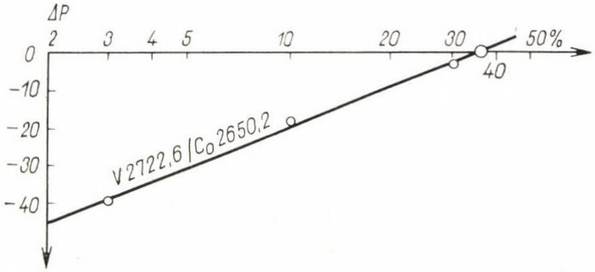

Fig. 3. Calibration curve for the determination of high concentrations of V. Measuring range 3.0—30.0 per cent

Nickel

For measuring low concentrations, also in the case of Ni one of the most sensitive atom lines, Ni 3414.7 was used, permitting a measuring within the concentration range from 0.005 to 1.0 per cent. For measuring high concentrations, the atom line Ni 3391.1 was selected, which gave from 1 per cent up to 30 per cent a very satisfactory calibration line. As reference line, the atom line Co 3431.6 was used with both lines. Thus, in the case of nickel, the whole concentration range can be measured with two pairs of lines.

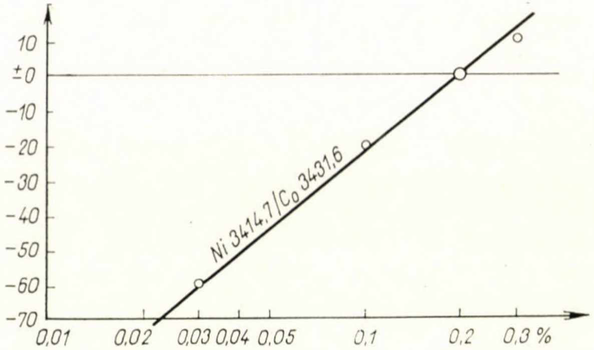

Fig. 4. Calibration curve for the determination of low concentrations of Ni. Measuring range: 0.005—1.0 per cent

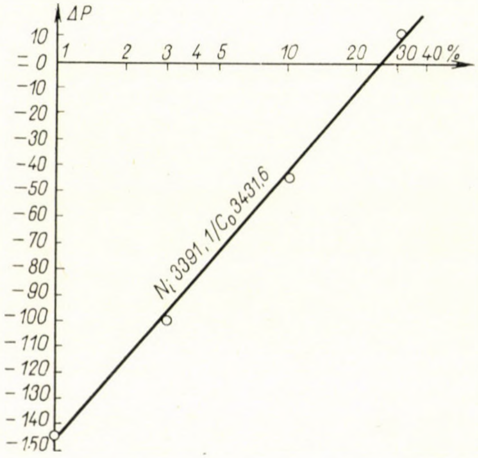

Fig. 5. Calibration curve for the determination of high concentrations of Ni. Measuring range 1.0—30,0 per cent

Working prescription

Excitation: BIG-100, low voltage, electronically controlled alternating current arc
Voltage: 220 V
Current: 4 A
Polarity: (+) (—)
Ignition: in each half period, at peak

Prearcing: 0 min.
Exposition: 1/2 min.
Spectrograph: Qu-24
Slit-width: 20 μ
Projection: intermediate
Spectral plate: *Agfa* Spektral Blau Extrahart, *Kodak* B10
Development: *Kodak* D 19, 18°C, 5 minutes, dish-method.

Pairs of analysis lines used in the method, and principal pertinent data are summarized in Table I. Calibration lines obtained with the five pairs of lines are shown in Figs 1—5.

Table I

Pairs of lines	Physical origin*	Transmission of spectral filter, %	Background correction	Measuring range %	Scattering rel. %
V 3185.4	I	100	+	0.005 — 0.6	4.0
Co 3062.2	I	100	∅		
V 3110.7	II	10	∅	0.6 — 10.0	7.0
Co 3062.2	I	100	∅		
V 2722.6	I	100	∅	3.0 — 30.0	—
Co 2650.2	I	100	∅		
Ni 3414.7	I	50	∅	0.005 — 1.0	2.5
Co 3431.6	I	50	∅		
Ni 3391.1	I	10	∅	1.0 — 30.0	5.5
Co 3431.6	I	50	∅		

* According to A. N. Saidel, V. K. Prokofjev and S. M. Raiski.

Thus, we succeeded in developing a spectrographic method, permitting the determination of both very low and relatively high V and Ni concentrations in oils with the same reliability. Referred to oil ash, the sensitivity of the method is 0.005 per cent of V and Ni, which, on assuming 0.01 per cent of ash content, corresponds to a sensitivity of half a millionth per cent, referred to the oil. Usually, no lower V or Ni content is met in crude oils.

According to our experiences, all of the calibration curves show only a minimum shift in the coordinate system on repeated photographs, so that in plant analysis, standard calibration curves may be used, and the whole evaluation process will be suited for computer programming.

SUMMARY

A method was developed for the spectrographic determination of V and Ni in the ash of Hungarian crude oils. Crude oils are first purified and dehydrated by centrifuging, and after this, distilled slowly in the presence of concentrated sulphuric acid. In this distillation, 10 to 20 drops of cc. H_2SO_4 are added to 100 g of oil, to prevent V and Ni losses. The ash is admixed in a proportion of 1 : 3 with SiO_2 powder containing 1 per cent of Co, and this mixture in a proportion of 1 : 2 with graphite powder of spectral purity. This spectrographic mixture is excited in the bore of a graphite electrode. The excitation parameters, the analysis and reference line used, together with the corresponding measuring ranges and reproducibilities are given. Referred to oil ash, the sensitivity of the method is 0.005 per cent, and its upper limit 30 per cent.

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ANALYSIS OF THE CONTAMINANTS IN NICKEL OF GRADED PURITY

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Introduction

A method has been developed for the activation analysis of telecommunication-grade nickel in order to assay the contaminants affecting the cathodic behaviour of nickel in electron tubes.

Nickel is one of the metals relatively seldom subjected to activation analysis. Though the determination of some elements in nickel has been already reported [1—7], no systematic analysis has been made of the contaminants of interest in cathode-grade nickel. The analytical method presented permits the quantitative determination of Cu, As, Zn, Sb, and Bi.

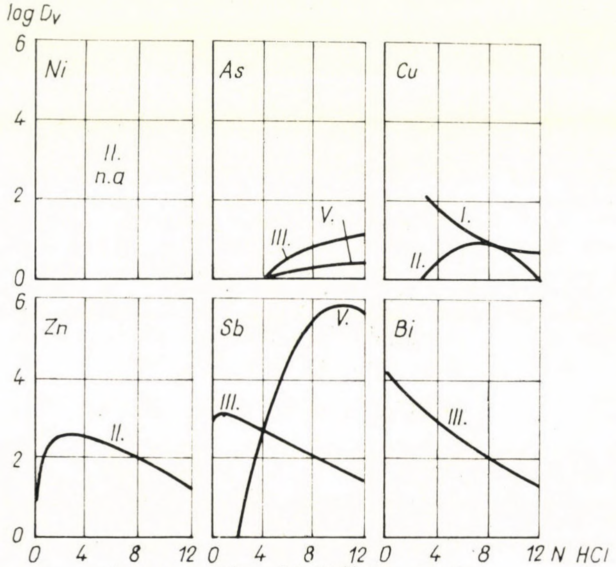
The use of non-destructive technique was impracticable because of the closely spaced γ-energies of the radioactivated isotopes of the elements to be determined. Moreover, owing to the relatively high activation of nickel, a further complication arises from the interference of the activities produced by the following nuclear reactions:

$$^{64}\mathrm{Ni}(\mathrm{n}, \gamma)^{65}\mathrm{Ni} \qquad t_{\frac{1}{2}} = 2.5 \ \mathrm{h}$$

$$^{58}\mathrm{Ni}(\mathrm{n}, \mathrm{p})^{58}\mathrm{Co} \qquad t_{\frac{1}{2}} = 70 \ \mathrm{d}$$

Of the available technique, ion exchange column chromatography seemed the most convenient for separation of the invidual elements from one another as well as from the main constituent nickel.

Fractionation by ion exchange offers the great advantage that nickel can be removed under favourable experimental conditions in a single step from the column, while the contaminants of interest can be eluted individually. Fractionation by ion exchange was performed on chloride-type *Dowex* 1×8 anion exchange column by exploiting the differences in the stabilities of the chloride complexes of the various contaminants involved. The volume distribution coefficients of the individual chloride complexes (D_v) in function of the hydrochloric acid concentration is shown in Fig. 1 [8]. As it is apparent from the figure, nickel does not form any chloride complex and can be washed out from the column with concentrated hydrochloric acid solution; on the other hand, each of the contaminants is bound by the column in the form of a chloride complex. Fractionation can be now achieved by elution in the order of successively increasing complex stability for arsenic, copper, and zinc, by means of hydrochloric acid of decreasing concentration and distilled water. The tightly bound Sb(III) ion has to be removed with a solution containing fluoride. The extraordinarily stable bismuth can be eluated only after having transformed the resin bed to sulphate form.



n.a. = not adsorbed from 0,1-12 N HCl solution

Fig. 1. Volume distribution coefficients of the individual chlorid complexes (D_v) in function of the hydrochloric acid concentration

The elements to be analyzed are separated from the fractions of rather large volume by precipitation. The activitives are measured on the precipitates, the precipitants being chosen such that no further purifying is necessary.

The following activites have been obtained:

Element	Half-life	Radiation involved
^{64}Cu	12.8 h	γ 0.51 MeV (annihilation radiation)
^{69m}Zn	13.8 h	γ 0.438 MeV
^{76}As	26.1 h	γ 0.55 MeV
^{122}Sb	2.8 d	γ 0.56 MeV
^{210}Bi	5.02 d	β

Experimental

Irradiation: Surface impurities were removed by dilute HNO_3 and distilled water; samples of about 0.1 g nickel metal measured and packed into quartz ampoule with cut-glass stopper were irradiated for 24 hours with about 10^{13} n/cm^2. sec neutron flux in one of the vertical channels of the *VVRS* research reactor. Nitrate standards of the elements in question were irradiated simultaneously for reference.

Dissolution of the irradiated sample. After irradiation, the nickel surface was cauterized by dilute HNO_3 to remove possible surface contaminants. The irradiated sample was then dissolved in a small volume of cc. HNO_3, evaporated and taken up with 5 ml of 12 *N* HCl containing 5 mg of each of the elements under investigation to act as carrier. $H_2N-NH_2 \cdot HCl$ was added to the solution to reduce antimony ions, to the trivalent state.

Ion exchange. A 50 mesh *Dowex* 1 × 8 anion exchange resin bed, 60 cm high and 0.7 cm in diameter, was used at a flow rate of 0.5 ml/min. Prior to ion exchange, the column was washed with cc. HCl. Nickel ions could be completely removed by passing 30 ml of 12 *N* HCl through the column. The individual elements were successively eluted as follows:

1. Arsenic	50 ml	6 *N* HCl
2. Copper	70 ml	2 *N* HCl
3. Zinc	50 ml	dist. water
4. Antimony	120 ml	1 *N* NaCl + 0.3 *N* NaF

After antimony had been eluted, sodium chloride and sodium fluoride were removed by washing the column with 50 ml of distilled water at maximum possible flow rate; using again the initial flow rate, the next step was to elute bismuth:

5. Bismuth	60 ml	2 *N* H_2SO_4

Individual treatment of the fractions

Arsenic:	Reduction to metal by sodium hypophosphite from the hot 6 *N* HCl solution.
Copper:	Precipitation in form of CuSCN from the solution that has been evaporated nearly to dryness, then diluted to 50 ml with distilled water. If the precipitate contains ^{58}Co activity, that has got into the copper fraction during ion exchange, it interferes with the activity measurement of less than 10^{-6} g copper is present; in this case the precipitation of CuSCN is repeated and the precipitate is then obtained in radiochemically pure form.
Zinc:	Precipitation as $ZnNH_4PO_4$.
Antimony:	Precipitation as Sb_2S_3 for activity measurement. The chemical yield was determined by converting the antimony sulfide into Sb_2O_4.
Bismuth:	Precipitation of Bi_2S_3 with 10% Na_2S from the neutralized solution.

Activity measurement

Copper, zinc, antimony and arsenic activites were measured with *Nuclear Enterprises 3"×3"* NaI(Tl) crystal coupled to a *KFKI Y-5-2-R* type, 128 channel pulse height analyser. Bismuth activity was measured with a GM counter.

Results

In the samples analyzed by the method described, the following contaminants were quantitatively identified: copper 10^{-6} g, antimony 10^{-9} g, arsenic 10^{-7} g, zinc 10^{-7} g and bismuth 10^{-6} g.

The γ-spectra obtained for the copper and arsenic fractions from both standard and sample are shown for comparison in Figs 2 and 3. It is seen that the radiochemical purity of the elements thus separated is quite satisfactory.

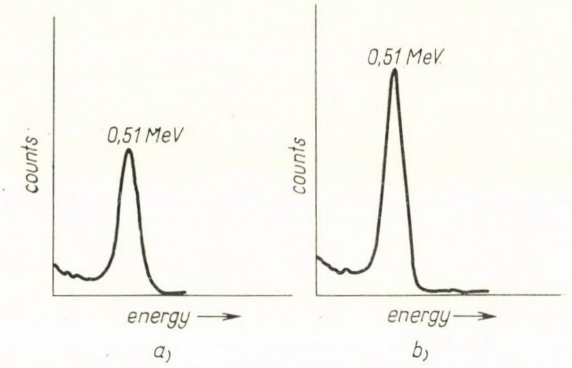


Fig. 2. a) Gamma spectrum of Cu standard; *b)* Gamma spectrum of Cu prepared from Ni sample

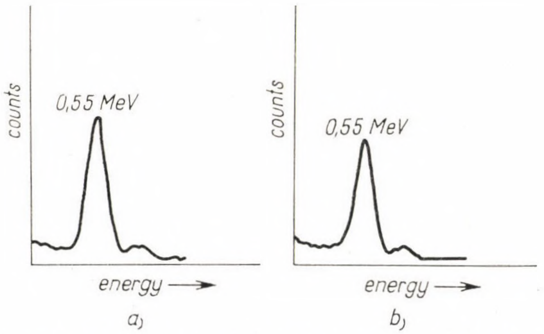


Fig. 3. a) Gamma spectrum of As standard; *b)* Gamma spectrum of As prepared from Ni sample

SUMMARY

A method of activation analysis of the contaminants of interest in telecommunication grade nickel is described. The individual elements are fractionated, after irradiation, by ion exchange. The technique is useful for the systematic analysis of arsenic, copper, zinc, antimony and bismuth.

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DETERMINATION OF THE COMPOSITION AND STABILITY CONSTANTS OF NITRITE COMPLEXES OF LEAD BY A POLAROGRAPHIC METHOD

(SHORT COMMUNICATION)

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The reduction of lead at the dropping mercury electrode has been studied by a number of workers in complexing and non-complexing media [1—4] and it was found that lead forms complexes with various complexing agents. During the polarographic reduction of lead in various supporting electrolytes, it was found that lead reduced reversibly, and the reduction is diffusion-controlled in sodium nitrite solution.

The present paper deals with the polarographic determination of composition and stability constants of complexes formed by lead with nitrite ion.

Experimental

All chemicals used were of reagent grade purity. The solution of lead was prepared by dissolving a weighed amount of lead nitrate in conductivity water, and standardised as usual. Sodium perchlorate was used to adjust constant ionic strength. Sodium nitrite was used as the complexing agent. *Triton* X_{100} (supplied by *Rohm and Haas Co.*) was used as maximum suppressor. A conventional H-type cell with agar-agar plug, saturated with sodium chloride was employed.

The measurements were made with a *L. P.* 55 HEYROVSKY system polarograph. The dropping mercury electrode had the following characteristics: $m = 2.12$ mg/sec. and $t = 3.6$ sec. (at -1.0 V *vs.* S. C. E. in 0.1 *M* potassium nitrate solution). All measurements were made $30 \pm \cdot 01$°C. For this purpose a HAAKE type ultrathermostat was used. Purified hydrogen was passed through the solution to remove dissolved oxygen. The reversibility of the reduction was tested by plotting log i/id-i *vs.* E_d. e.

Solutions containing 1 millimole of Pb^{2+} and 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 or 1.0 mole of sodium nitrite, respectively, were prepared. The ionic strength ($\mu = 1.0$) was kept constant by adding the required amount of sodium perchlorate solution. *Triton* X_{100} (0.001%, in the final solution) was added to suppress the maximum. The polarograms were recorded manually after deaeration.

Theory

It was shown by DEFORD and HUME [6] that the shift in half-wave potential due to complex formation can be expressed as follows:

$$\Delta E_{\frac{1}{2}} = (E_{\frac{1}{2}})_c - (E_{\frac{1}{2}})_s = \frac{2.303\,RT}{nF} \log Y \frac{I_c}{I_s} \sum_0^N \frac{\beta_j \{X\}^j}{Y_{MX}} \tag{1}$$

where $(E_{\frac{1}{2}})_c$ and and $(E_{\frac{1}{2}})_s$ are the half-wave potentials of the complex and simple metal ions, respectively; R, T and F have their usual significations; n denotes the number of electrons; I_s and I_c are the experimental diffusion constants for the simple ion and for all complex ions, respectively; β_j is the overall formation constant of the j^{th} complex; $\{X\}$ is the activity of the complexing ligand, while Y_M and Y_{MX} denote the activity coefficients at the electrode surface of the metal and complex species, respectively. Equation (1) can be rearranged to define a function F_0 ($[X]$) such that:

$$F_0([X]) = \text{antilog}\left(\frac{0{,}43\,nF}{RT}\,\Delta E_{\frac{1}{2}} + \log\frac{I_s}{I_c}\right) = Y_M \sum_0^N \frac{\beta_j\{X\}^j}{Y_{MX}}$$

$$= 1 + \beta_1\,[X]\,\frac{Y_M Y_X}{Y_{MX1}} + \beta_2\,[X]^2\,\frac{Y_M (Y_X)^2}{Y_{MX2}} + \ldots \tag{2}$$

$$F_1([X]) = \frac{F_0([X]) - \beta_0/Y_s}{C_X\,Y_X} \tag{3}$$

$$F_2([X]) = \frac{F_1([X]) - \beta_1/Y_{MX}}{C_X\,Y_X} \tag{4}$$

$$F_3([X]) = \frac{F_2([X]) - \beta_2/Y_{MX2}}{C_X\,Y_X} \tag{5}$$

where $[X]$ denotes the concentration of the complexing ligand and Y_X is the corresponding activity coefficient. Values of F_0 ($[X]$) for different concentrations of the complexing ligand can be determined experimentally, and Equation (2) can then be solved graphically for β_1, β_2 and β_3.

Further calculations show that the ratio of the uncomplexed metal ion to the various complex species as a function of the ligand concentration can be obtained from the following equations:

$$\frac{[M]}{C_M} = \frac{1}{F_0([X])} \tag{6}$$

and

$$\frac{[MX_j]}{C_M} = \frac{\beta_j [X]^j}{F_0([X])} \tag{7}$$

where $[M]$ denotes the concentration of uncomplexed metal ions, $[MX_j]$ = the concentration of the j^{th} complex species, and C_M = the total metal ion added to the system.

Results and discussion

In each case, a single, well defined reduction wave was obtained; the shift of the half-wave potential towards a more negative value with increasing concentration of nitrite ion indicates the formation of complexes between lead and nitrite ion. The diffusion current was found to decrease regularly with the increase of nitrite ion concentration. This is due to the change in the size of the particle which takes place owing to complex formation. The complex ions formed are much larger than the aqueo-metal ion, hence they have a low diffusion coefficient, resulting in a decrease of the diffusion current as the concentration of the complexing agent is increased.

The plots of log i/i_d-i vs. Ed. e. are linear with a slope of the order of 31 ± 2 mV, indicating the reversibility of the reduction. The value of 'n' is found to be 2.

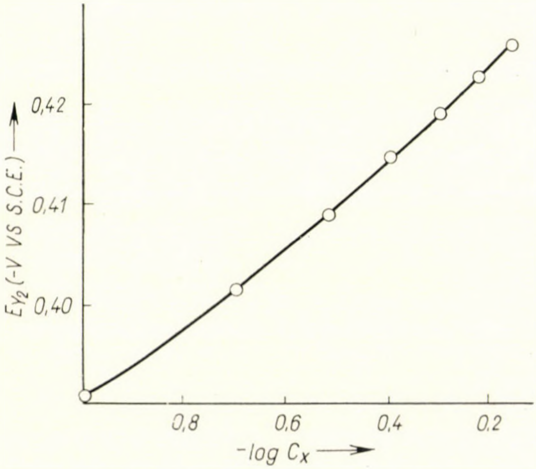

Fig. 1. Plot of $E_{\frac{1}{2}}$ *vs.* Log C_x

The plot of $E_{\frac{1}{2}}$ vs. $-\log C_X$ ($C_X =$ nitrite ion concentration) gives a smooth curve (Fig. 1), showing the formation of two or more complex species which are in equilibrium. The classical method of LINGANE [5] could not be applied. Therefore, DEFORD and HUME's method [6] modified by IRVING [7] has been adopted. The values of the overall formation constants were calculated by graphical extrapolation. The experimentally determined values of the half-wave potentials, together with the F_j ([X]) values calculated from Equations (1), (2), (3), (4) and (5) are given in Table I. The overall formation constants were obtained by extrapolation of the F_j ([X]) functions to zero ligand concentration (Fig. 2). Three complex species, $Pb(NO_2)^+$, $Pb(NO_2)_2$ and $Pb(NO_2)^-_3$, were found to be present having the overall formation constants 85, 227 and 135, respectively.

Table I

Analysis of the function F_j ([X])

Cg (moles)	$E_{\frac{1}{2}}$ (—V vs. S. C. E.)	i_d (divisions)	Slope (mV)	F_0 ([X])	F_1 ([X])	F_2 ([X])	F_3 ([X])
0.0	0.3802	63	32				
0.1	0.4062	63	30	9.875	88.75	—	—
0.2	0.4186	61.5	33	19.38	96.9	—	—
0.3	0.4267	61	31	36.39	117.9	127	—
0.4	0.4348	61	32	67.79	166.9	204.7	—
0.5	0.4392	60.	32	96.40	190.8	211.6	—
0.6	0.4462	60	30	164.9	273.1	313.5	144.1
0.7	0.4495	59.5	30	213.7	303.8	312.5	122.1
0.8	0.4528	58	32	280.2	349.0	335.0	135.0
0.9	0.4557	58	30	350.95	395.5	345.0	131.0
1.0	0.4587	58	30	444.5	443.5	358.5	131.5

The percentage distribution of lead present in various forms as a function of the logarithm of nitrite ion concentration has been calculated by Equations (6) and (7), and the results are presented in Fig. 3.

Since the reduction of lead is diffusion-controlled, lead can be determined polarographically in nitrite solution.

The authors wish to express their thanks to *University Grants Commission*, New Delhi for granting a Junior Fellowship to one of them (D. S. J.) and to the Head of the *Chemistry Department* for providing facilities.

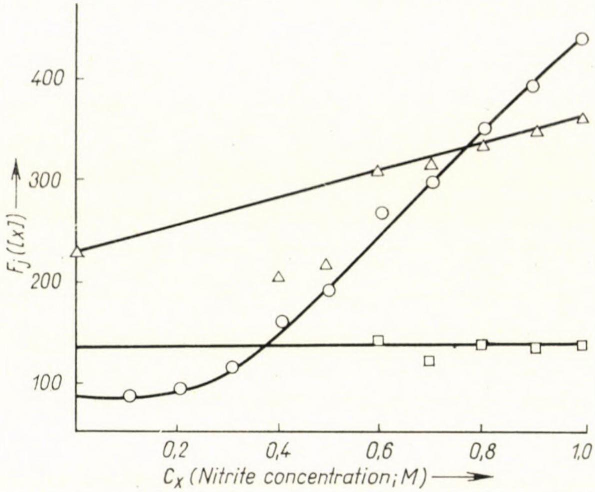

Fig. 2. F_j ($[x]$) plots for lead-nitrite system: [○], F_1 ($[x]$); [△], F_2 ($[x]$); [□], F_3 ($[x]$)

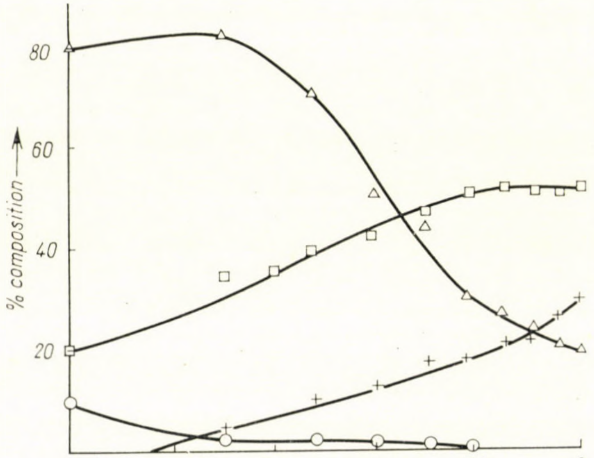

Fig. 3. Percentage composition for various species of lead-nitrite system: [○], Pb^{2+}; [△], $Pb(NO_2)^+$; [□] $Pb(NO_2)_2$; [+], $Pb(NO_2)^-_3$

SUMMARY

The reduction of lead in nitrite solution at the dropping mercury electrode has been studied. The reduction is reversible and diffusion-controlled. The shift of the half-wave potential towards a more negative value with the increase of nitrite concentration indicates complex formation. The composition and stability constants have been calculated by DeFord and Hume's method. Three complex species ($Pb(NO_2)^+$, $Pb(NO_2)_2$ and $Pb(NO_2)^-_3$ were found to be present with the overall formation constants 85, 227 and 135, respectively. The percentage distribution of lead present in the various forms as the function of nitrite concentration is presented.

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ANALYTICAL USES OF 1 : 2 DIAMINOCYCLOHEXANETETRA-ACETIC ACID (CDTA) — DETERMINATION OF Pb^{2+} AND Tl^{+} IN PRESENCE OF EACH OTHER BY POLAROGRAPHY AND AMPEROMETRY

(SHORT COMMUNICATION)

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In supporting electrolytes, which do not complex lead ions, the thallium and lead waves coincide. The half-wave potentials of lead and thallium ions in $1M$ potassium nitrate have been found to be —0.40 V *vs* S. C. E. 1 and —0.48 V *vs* S. C. E. [2] respectively, at 25°C and thus their polarographic determination in presence of each other presents some difficulty. WINN [3] has determined thallium in presence of lead in a sample of urine by treating the sample with a mixture of sulphuric, perchloric and nitric acid. Thallous was oxidised to thallic with bromine water and then extracted with a chloroform solution of dithizone, while lead remained in the aqueous phase under these conditions. Thallium was estimated from the choloroform extract. The present paper reports a method by which lead and thallium can be determined in presence of each other amperometrically and polarographically, without oxidising thallous to thallic ion (using CDTA).

Experimental

All the chemicals used were of reagent grade purity. Redistilled water, distilled in all pyrex glass apparatus was used during all the experiments. The purity of the sample of CDTA, as supplied by L. *Light and Co.* was checked by titrating it against a standard solution of zinc, using *Eriochrome Black* T as indicator [4]. The sample was found to be cent percent pure.

L. P. 55 HEYROVSKY system polarograph was used manually. The dropping mercury electrode had the following characteristics: $m = 1.76$ mg/sec. and $t = 4.6$ sec. (at —1.0 V *vs* S. C. E. in 0.1 M potassium chloride solution). All the measurements were done at 25 ± · 01°C which was controlled by a HAAKE type ultra thermostat. The pH of the solution was measured by a bench type battery operated *Cambridge* pH meter. *Triton* X_{100} was used as a maximum suppressor. Purified hydrogen was passed through the solution for deaeration. In case of amperometric titrations, the supply of gas was cut off during the actual measurements and after each addition of the titrant, the gas was passed for a minute. The other details of the amperometric titrations have been given elsewhere [5].

Results and discussion

Determination of lead in presence of thallium (ous): Since at pH 5.0, Tl^+ does not complex with the anion of CDTA, it is possible to titrate Pb^{2+} with CDTA amperometrically in presence of Tl^+. The pH of the solution was kept at 4.5, by adding perchloric acid and sodium hydroxide solution. In this medium, lead reduces sooner than Tl^+, so at an applied voltage of -0.4 V *vs* S. C. E. only Pb^{2+} is reduced at the dropping mercury electrode, and can be titrated against standard solution of CDTA.

Solutions containing different amounts of Pb^{2+} and Tl^+ were prepared and analysed amperometrically by titrating against a standard solution of CDTA (0.01M). The results have been recorded in Table I.

Table I

Amperometric titration of Pb^{2+} in presence of Tl^+ with CDTA (0.01M)

P^{2+} (0.025M) present in mixture (ml)	Tl^+ (0.025M) present in mixture (ml)	Volume of CDTA required (ml)	Pb^{2+} found (ml)
0.8	1.0	2.0	0.8
1.0	1.0	2.45	0.98
1.0	2.0	2.48	0.992
1.6	2.0	4.08	1.63
0.4	2.0	1.0	0.4

Determination of Tl^+ in presence of Pb^{2+}:

(a) *Amperometrically:* In this case solutions containing different amounts of Pb^{2+} and Tl^+ were prepared and excess of CDTA was added and the pH of the solution was adjusted to 5.5. At this pH, lead is masked by CDTA, forming a complex which is non-reducible. Only a single reduction wave due to the reduction of Tl^+ appeared ($E = -0.46$ V *vs* S. C. E.). Thus it was titrated amperometrically with standard solution of potassium chromate at an applied voltage of -0.56 V *vs* S. C. E. [6] The results have been incorporated in Table II.

(b) *Polarographically:* The above determination can also be made polarographically. Solutions containing different amounts of Tl^+ and Pb^{2+} (pH 5.5) were prepared and CDTA was added in excess and polarographed. The single reduction wave appeared for reduction of Tl^+. The wave height was measured and the concentration was calculated by the standard comparison method, taking a polarogram of Tl^+, whose concentration is known under similar conditions. The results have been reported in Table III.

The percentage error in all the cases was of the order of ± 2.

Table II

Amperometric titration of Tl^+ in presence of Pb^{2+} with potassium chromate (0.1M)

Tl^+ (0.025M) present in mixture (ml)	Pb^{2+} (0.025M) present in mixture (ml)	Volume of K_2CrO_4 used (ml)	Tl^+ found (ml)
1.0	0.5	1.25	1.0
2.0	1.0	2.5	2.0
2.0	2.0	2.55	2.04
4.0	2.0	4.95	3.98
0.8	1.0	1.0	0.8
0.4	1.0	0.49	0.392

Table III

Polarographic determination of Tl^+ in presence of Pb^{2+}

Tl^+ (0.025M) present in mixture (ml)	Pb^{2+} (0.025M) present in mixture (ml)	Tl^+ found (ml)
1.0	2.0	1.0
2.0	2.0	2.0
0.8	1.0	0.79
0.4	1.0	0.395
1.0	0.8	1.02
0.4	1.6	0.404

SUMMARY

The present paper deals with the determination of lead and thallium in presence of each other by a polarographic and amperometric method. Lead was determined in presence of thallium by titrating it against standard solution of CDTA amperometrically at pH 4.5, since at this pH, thallium does not complex with CDTA. Whereas, thallium in presence of lead was determined at pH 5.5, by titrating it against standard solution of potassium chromate, lead was masked with CDTA. The same was also carried out by a polarographic method. The error is about ± 2%.

The authors wish to express the thanks to the U. G. C. for granting a Junior Research Fellowship to one of them (D. S. J.) and to Prof. R. C. MEHROTRA, Head of Chemistry Department for providing facilities.

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A THEORY OF SOME PHOTOCHEMICAL PROCESSES AT CRYOGENIC TEMPERATURES

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Introduction

Cryogenic photolysis of organic compounds originated in 1941 with the work of Lewis and Lipkin [1] on hexaphenylethane and tetraphenylhydrazine. Subsequently, nothing was done until, in 1954, Norman and Porter [2] and Whittle, Dows and Pimentel [3] published simultaneously. These latter workers were interested in the kinetically significant reactive radicals known to occur in solution and in the gas phase, in contrast to the stable Gomberg type radicals of Lipkin *et. al.*, and the subsequent intense activity in the field must be credited to their efforts.

The greater part of the published work up to this time relates to spectroscopic studies and little information of value as to the stable products of photolysis is to be found. Almost without exception, it has been assumed that photolysis initially follows the pattern of the gas and liquid phases, thus *e.g.*

$$RX + h\nu \rightarrow R\cdot + X\cdot$$

the radicals formed then reacting "normally" except in so far as the solid environment affects the kinetics. In general, the expected radicals have been observed in the systems and unquestionably, much has been learnt about them. However, it is questionable whether much has been learnt about photolytic mechanisms in cryogenic systems and in the few instances where mechanisms have been postulated these are merely extensions of gas or liquid phase schemes.

Detailed study of the spectroscopic data and the few available (and almost entirely qualitative) analytical product data suggest numerous anomalies. To cite a few examples only. In the photolysis [4] of HI in Ar at 4°K, e. s. r. study reveals three doublets, one of which corresponds to the free H atom. In the photolysis [5] of CH_2N_2 in CO at 20 °K, ketene is a product. Finally, in the photolysis [6] of CH_3NO_2 in Ar at 20°K, infra-red spectra reveal the presence of the products CH_2O, CO, CO_2, N_2O, NO, HNCO, H_2O and NH_3. There might obviously be many more. Briefly, it is clear that

(i) even the most unlikely matrices are not to be regarded as inert in every circumstance;

(ii) since analytical data are scarce, the product complexity observed with CH_3NO_2 may be a general phenomenon.

The latter proposition is particularly significant since, as Pimentel has pointed out [7], and our own studies [8—10] entirely support this, all the evidence points to cage localisation of reactive species and hence, all chemistry must occur at the site of photon absorption. The H atom and aromatic radicals may have to be exempted to some extent, the former because of high diffusivity, the latter because their stability makes up for slow diffusivity. If, therefore, radicals which may be formed cannot leave the cage of formation, product complexity becomes difficult to explain. Brown and Pimentel, in fact, were forced to propose four successive photon absorptions in the same cage to account for some of the products of CH_3NO_2 photolysis. This is a questionable and uneconomical hypothesis.

Present work

The work outlined here was based on the propositions (i) and (ii) quoted above. Thus, with the wealth of spectroscopic information available, it is suggested that attention is now better concentrated on the use of the powerful analytical techniques now at hand and the use of matrices, reactive in known ways. We have developed a photolytic system incorporating high speed, high sensitivity gas chromatography of our own design. Details are given elsewhere [9]. The systems so far studied are listed in Table I.

Table I

Photolytic systems studied at 77 °K

Irradiation by 2537A light

Matrix	Reactants	Collaborator
C_2H_4	HI, CH_2I_2, CH_3I, C_2H_5I, n—C_3H_7I, CH_3HgCH_3	Hughes [8—10]
C_3H_6	HI, CH_3I, C_2H_5I, CH_2I_2.	Hughes [9, 10] Hughes[12] and Young [11]
Allene	HI	Hughes [8]
Cyclopropane	HI. CH_3I, CH_2I_2	Hughes [8] Young [11]
C_2H_4	CH_3NO_2, CH_3ONO, CH_3COCH_3.	Young [11]

The most detailed quantitative work has been that on the systems C_2H_4—HI and C_3H_6—HI, these have been discussed elsewhere in detail [9]. Because of limitations of space these will not be repeated and it is proposed here also only to present a selection of results for other systems sufficient to develop discussion.

Photolysis of CH_3I in various matrices

This photolysis has proved to be of outstanding interest because of the unexpected nature of some of the products.

Table II lists a typical set of results.

Table II

2537 Å photolysis of CH_3I at 77°K
Photolysis time = 40 min. Film thickness $\simeq 10^{-5}$ cm

Product	$CH_3I/C_2H_4 = 45/9$ (μmoles)		$CH_3/C_3H_6 = 45/9$ (μmoles)	
Methane	80	100%(A)	90	100%(C)
Ethane	20		8	
Ethylene	—		2	
Propane	4	100%(B)	1%(C)	
Propylene	49			
Cyclopropane	47			
n-Butane			5	100%(D)
Iso-butane			5	
Methylcyclopropane			40	
But-l-ene			32.5	
Isobutene			6	
cis-But-2-ene			3.5	
tr-But-2-ene			2.5	
Butadienes			5.5	
	(A) = 4 (B)		(C) = 6.25 (D)	

The films were made deliberately rich in CH_3I because of the desire for certainty of measurement of the tiny yields of products. Hence, product groups (A) and (C) are essentially those of undiluted CH_3I photolysis. Products (B) and (D) however, whose yields relative to (A) and (C) can be increased by more favourable CH_3I/olefin ratios, are those of reaction with the matrix. At once, it is seen that, in both olefins, the predominant new product is cyclic and this, at first sight would seem to prove the presence of CH_2 radicals, since these readily add cyclically across a double bond. However, some higher saturates are also formed and all higher olefins, in principle, could come via $CH_3^{\cdot}$ *e.g.*,

$$CH_3I + h\nu \rightarrow CH_3^{\cdot} + I \quad \text{(a)}$$

$$CH_3^{\cdot} + C_3H_6 \rightarrow C_4H_9^{\cdot} \quad \text{(b)}$$

$$C_4H_9^{\cdot} + I \rightarrow C_4H_8 + HI \quad \text{(c)}$$

reactions of types (a) and (c) being generally cited as the major reactions in alkyl iodide photolysis at low temperature. Thus, on the conventional view, we would be forced to assume the possibility at least that at 77°K the reaction (a), and to explain the results, the direct methylene forming step

$$CH_3I + h\nu \rightarrow CH_2 + HI \tag{d}$$

were about equally likely.

Some important information comes also from products which are not formed. Thus, cyclobutane is not produced in C_3H_6 matrices, which indicates a three centre transition state for cyclisization. Again the dimers of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, $C_3H_7^{\cdot}$ and $C_4H_9^{\cdot}$ are absent, which clearly establishes localisation of the radicals. Since radical combination is thereby eliminated, so too is disproportionation as a source of olefins. Finally, alkyl iodides occur only in trace amount [$< 1\%$ (B) or (D)]. This indicates that reactions such as

$$R^{\cdot} + I \rightarrow RI \tag{e}$$

are trivial, which would be surprising if substantial amounts of $R^{\cdot}$ were formed in thermal equilibrium. There is strong evidence that but radicals are not involved [7, 8, 9] to any great extent in aliphatic photolyses and in this connexion it is notable that in this work no products of H abstraction from olefins have been found in any system; the activation energy would in general not exceed 5—8 kcal mole^{-1}, which contrasts with the initial energy of 112 kcal · mole^{-1}.

To explain these and other results, HUGHES and PURNELL [8—10] have proposed that, in fact, initial photolysis produces not the obvious radicals as in (a) or (d) but a highly energised ($\leqslant$ 112 kcal · mole^{-1}) complex involving the photo-absorber with any molecules which may be present in the matrix. Thus, *e.g.* with absorber RX,

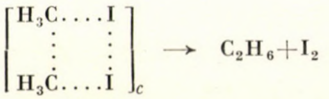
$$[RX + M + h\nu]_c \rightleftarrows [R\ldots X\ldots M]_c \tag{1}$$

The energised complex is indicated by dots within a bracket and the cage by the subscript c. The molecule M represents any matrix component including RX. The complex is visualised as loose, with reasonably free rotation of the parts, a view consistent with e. s. r. findings regarding CH_3I photolysis [13]. Then, for example, in the photolysis of CH_3I we could visualise at least two states of CH_3I in relation to the matrix molecule following absorption *viz.*

(I) $H_3C \ldots . I$ or (II) $H_2C \ldots H \ldots I$

Forms (I) and (II) would, of course, interchange rapidly through methyl rotation and excitation of C—H vibrations.

In photolysis of pure CH_3I we could then have the following possibilities



$$\begin{bmatrix} H_3C\cdots I \\ \vdots \qquad \vdots \\ H_3C\cdots I \end{bmatrix}_c \longrightarrow C_2H_6 + I_2 \tag{f}$$

$$[I\ldots H\ldots CH_2\ldots CH_2\ldots H\ldots I]_c \rightarrow C_2H_4 + 2\,HI \tag{g}$$

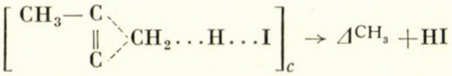
$$[I\ldots CH_2\ldots H\ldots CH_3\ldots I]_c \rightarrow [ICH_2]_c + CH_4 + [I]_c \tag{h}$$

$$[I\ldots CH_3\ldots I\ldots CH_3]_c \rightarrow CH_3I + [I + CH_3]_c \rightarrow 2\,CH_3I \tag{i}$$

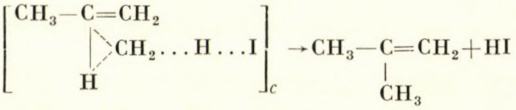
$$[CH_3\ldots I\ldots I\ldots CH_3]_6 \rightarrow [CH_3^{\cdot}]_c + I_2 + [CH_3^{\cdot}]_c \tag{j}$$

These reactions are written pictorially and the configurations must not be taken too literally. Reactions (f)—(h) lead to the observed products, reactions (ij) yield the methyl radicals observed in e. s. r. and also account for the low quantum yield ($\Phi \simeq 0.05$). Reaction (h), interestingly, produces fragments in different cages and hence should stabilise $[\cdot CH_2I]$.

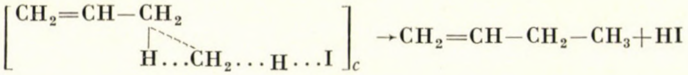
In the presence of added olefin *e.g.* C_3H_6 we have the added possibilities;



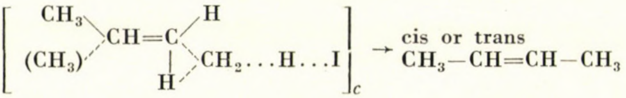
$$\left[\begin{matrix} CH_3-C \\ \quad \| \\ \quad C \end{matrix} \rangle CH_2\ldots H\ldots I\right]_c \rightarrow \Delta^{CH_3} + HI \tag{k}$$



$$\left[\begin{matrix} CH_3-C=CH_2 \\ \quad\ | \\ \quad H \end{matrix} \rangle CH_2\ldots H\ldots I\right]_c \rightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + HI \tag{l}$$

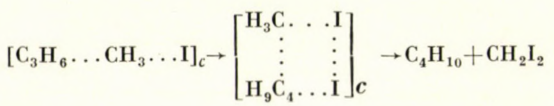


$$\left[\begin{matrix} CH_2=CH-CH_2 \\ H\ldots CH_2\ldots H\ldots I \end{matrix}\right]_c \rightarrow CH_2=CH-CH_2-CH_3 + HI \tag{m}$$



$$\left[\begin{matrix} CH_3 \\ (CH_3) \end{matrix} \rangle CH=C \begin{matrix} H \\ | \\ H \end{matrix} \rangle CH_2\ldots H\ldots I\right]_c \rightarrow \begin{matrix} \text{cis or trans} \\ CH_3-CH=CH-CH_3 \end{matrix} \tag{n}$$

The formation of butanes can be similarly written, for convenience we summarise,



$$[C_3H_6\ldots CH_3\ldots I]_c \rightarrow \begin{bmatrix} H_3C\ldots I \\ \vdots \qquad \vdots \\ H_9C_4\ldots I \end{bmatrix}_c \rightarrow C_4H_{10} + CH_2I_2 \tag{o}$$

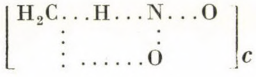
the second CH_3I shown in the bracket being readily available in CH_3I rich matrices at least.

It is seen that the reactions of $CH_2\ldots H\ldots I$ are formulated similarly to the well known methylene insertion process and they thus pose no particular difficulty of visualisation. Support for this view comes from photolyses in cyclopropane matrices when methyl cyclopropane is an abundant product. Thus, methylene insertion certainly occurs in the system by some mechanism.

The general postulate offered has been shown [9] to account both for the concentration dependence of product formation in HI-olefin photolyses and also for the qualitative details of HI — cyclopropane or allene [8] photolyses. In extension of the hypothesis it can be seen that the complex products of *e.g.* CH_3NO_2 photolysis can be well explained since a number of formal structures,

(III) $[CH_3\ldots NO_2]_c$ (IV) $[CH_3\ldots O\ldots N\ldots O]_c$

(V) $[H_2C\ldots H\ldots NO_2]_c$ (VI)



$$\left[\begin{array}{l} H_2C\ldots H\ldots N\ldots O \\ \quad\;\vdots \qquad\qquad\;\; \vdots \\ \quad\;\vdots\;\ldots\ldots O \end{array}\right]_c$$

among others, can be written and these, with others, offer simple routes by decomposition to most of the observed compounds. Our studies with CH_3NO_2 and CH_3ONO in olefins show that, as with CH_3I, cyclic products are abundant and, in this instance, the proposition that free methylene is produced via

$$CH_3NO_2 + h\nu \rightarrow CH_2 + HNO_2$$

$$CH_3ONO + h\nu \rightarrow CH_2 + HONO$$

is far less easy to support than is reaction (d). Photolyses of CH_3NO_2 and CH_3ONO in cyclopropane also yield methylcyclopropane in good yield. Again, therefore, we have evidence of the equivalent of methylene insertion as visualised in reactions (k) and (n).

The present hypothesis is no more than qualitative but has at least the merit of economy. Invoking only the minimum number of kinetic and photochemical steps it accounts for all the analytical evidence available for cryogenic photolysis of aliphatic compounds; it allows the total acceptance of cage localisation; it explains the absence of hot radical effects and, finally, it focusses attention on the point that gas phase mechanisms may bear no relation to events in solid films and, thus that the sometimes difficult task of reconciling such data may be fruitless.

Since this work was first done, the photolysis of methylene iodide in liquid cyclohexene [14] has been shown to yield norcarane as a minor product; an explanation similar to ours has been found to be the only reasonable one. Thus, clearly cryogenic photolysis studies may help clarify the mechanisms of the liquid state besides. In conclusion, it is seen that if our general hypothesis is correct, cryogenic photochemistry offers a whole new area for study and many unexpected reactions may be anticipated.

SUMMARY

Recent analytical studies of the products of photolysis of HI and HC_3I in reactive hydrocarbon matrices at 77°K are reviewed and it is suggested that the results are more consistent with photolysis of loose absorber-matrix complexes than of absorber molecules alone. The structure of possible complexes of the type $[R-I]_2$ and $[RI-M]$ which could give rise to the observed products are indicated and the theory is extended to offer a qualitative explanation of the origin of the products of cryogenic photolyses of CH_3NO_2 and of CH_3ONO.

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RELATIONSHIP BETWEEN BOND STRENGTHS AND VIBRATIONAL FORCE CONSTANTS

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In its generalized form, the potential energy function contains a number of stretching and angle deformation members connected by different interaction terms [1]. If the force field of a given molecule is represented in matrix form, its leading diagonal members can be said to be most characteristic for vibrational behaviours.

The setting up of potential functions is a many body problem that in most cases cannot be solved exactly. Theoreticians in this field have to use experimental data for energy calculations. Spectral data serve as experimental values to set up the expressions for the potential energy. It often occurs that the equations we have are quantitatively or qualitatively insufficient for the determination of a force field hence approximate solutions have to be used [2]. As starting-points for the application of iterative methods, the empirical potential energy functions and thus the force constants of diatomic molecules can be used as zero order approximations for the calculations of force fields in polyatomic molecules.

In this manner we are able to attribute a certain physical meaning to the stretching part of the potential energy equations indicative of the dependence existing between force constants and dissociation energy expressions.

This paper is restricted to the treatment of the potential energy function of diatomic and of the stretching part of the potential energy function of simple polyatomic molecules.

It is known that certain physico-chemical properties of polyatomic molecules may be deduced from certain parameters connected with their bonds. On the other hand, such parameters can be obtained with sufficient accuracy by using certain experimental values of the corresponding diatomic molecules. Such an approach seems to be suitable also for calculating the stretching force constants of polyatomic molecules.

The application of this concept is well justified by the following facts:

1. The values of the fundamental stretching frequencies of certain diatomic molecules may be very similar to those of the corresponding bonds existing as component parts among other valence parameters of a polyatomic molecule.

2. The dissociation energies of diatomic molecules are often found to be only slightly different from the energies required for the breaking of similar bonds in simple polyatomic molecules.

In the case of diatomic molecules there is a relationship between the vibrational potential energy coefficients (force constants) and the bond strengths [3]. In the course of the last few decades a number of appropriate empirical potential functions have been published [4], however nearly all expressions proposed so far are somehow connected with the periodic system.

In the numerous theoretical or semiempirical formulations occurring in the literature mostly the attraction and repulsion terms are responsible for the values of bond length, ionization potential, electronegativity and for many other molecular properties [5]. A closer investigation of this fact suggested the possibility that the potential energy function for a diatomic or simple polyatomic system might be determined by using other measured physicochemical data instead of vibrational frequencies.

The great majority of the empirical potential energy expressions published so far has been restricted to certain selected types of molecules with the purpose to achieve agreements much better than one per cent between different experimental and calculated values.

However, the reliability of the experimental values given in the literature is in many cases questionable as numerous contradictions may be found between the data obtained by different methods and authors [6]. Some important experimental data *(e.g.* dissociation energies) simply cannot be measured, even now, accurately enough. Further problems arise in connexion with the fundamental experimental data of the vibrational spectra because of anharmonicity or other difficulties occurring.

By reason of the facts mentioned above it was considered justifiable to accept a poorer agreement between our experimental and calculated values, if in turn we succeeded in constructing a potential energy formula involving only parameters in their simplest form.

In the following, we propose — at the price of gross neglections — an expression for the stretching part of potential energy formulas, in which though the terms depend on the periodic system they also maintain their peculiar character.

We propose the following expression for the empirical potential energy function of a diatomic molecule:

$$\bar{U} = \bar{D}_e \left[1 - \exp\left(- \frac{(r - r_e)^2 \, de \, \bar{D}_e^{-1/2}}{2r} \right) \right] \tag{1}$$

where $\bar{D}_e$ stands for the equilibrium dissociation energy, e denotes the geometrical mean of the electronegativities of atoms forming the bond, d is a proportionality constant, r_e is the equilibrium interatomic distance, and r is the displacement. $\bar{U}$ and $\bar{D}e$ refer to unit valency.

The force constant can be obtained in the usual way as the second derivative at $r = r_e$:

$$k_e = \frac{de\,\bar{D}_e^{1/2}}{r_e} \tag{2}$$

Denoting by i and j the constituent atoms of a bond, we generalize this result as follows:

$$\bar{k}_{ij} = d_{ij}\,(e_i\,e_j)^{1/2}\,\bar{D}_{ij}^{1/2}\ \ r_{ij}^{-1}$$

where $\bar{k}_{ij}$ and $\bar{D}_{ij}$ denote the force constant and the dissociation energy both referring to unit valency (for the sake of simplicity, the lower index e has been omitted).

We supposed:

$$d_{ij} = (d_i\,d_j)^{1/2} \tag{3}$$

where d_{ji}-s are values for heteronuclear molecules and d_j, d_i for homonuclear ones. Some examples will be given in the following five tables.

In Table I data of homonuclear diatomic molecules are shown. The d values range from 0.26 to 0.3. The N_2 molecule has a value too high, due to the exceptional high dissociation energy.

Table I

	k_e	r_e	$(e_1e_2)^{\frac{1}{2}}$	$\bar{D}_{ij}$	d_{ij}
C_2	9.51	1.312	2.5	68.5	0.301
O_2	11.76	1.207	3.5	58.5	0.265
S_2	4.96	1.889	2.5	50.9	0.263
F_2	4.453	1.435	4.0	36	0.266
Cl_2	3.279	1.988	3.0	57.1	0.287
Br_2	2.457	2.284	2.8	45.5	0.298
I_2	1.721	2.667	2.5	35.6	0.308
N_2	22.96	1.094	3.0	75.0	0.322
P_2	5.56	1.894	2.1	38.7	0.268

In Table II diatomic molecules containing hydrogen atom are to be seen. It is expected that d-s have particular values because of the bonding character of hydrogen molecules. In spite of this expectation the mean value does not

deviate from the average of other molecules of predominantly covalent character.

Table II

	k_e	r_e	$(e_1e_2)^{\frac{1}{2}}$	D_{ij}	d_{ij}
CH	4.482	1.120	2.29	80.0	0.245
NH	6.030	1.038	2.51	93.5	0.258
PH	3.257	1.433	2.10	77.0	0.254
OH	7.792	0.971	2.71	101.0	0.278
SH	4.193	1.350	2.29	85.0	0.268
FH	9.655	0.917	2.90	135.0	0.263
ClH	5.157	1.275	2.51	102.0	0.259
BrH	4.117	1.414	2.42	85.5	0.260
IH	3.142	1.604	2.29	70.5	0.263
BH	3.044	1.232	2.05	60.0	0.236
SiH	2.479	1.521	1.94	58.0	0.254
GeH	1.87	1.66	1.94	38,0	0.260
AsH	2.43	1.58	2.05	56.0	0.252
SeH	3.18	1.50	2.24	67.0	0.260
TeH	2.53	1.69	2.10	59.0	0.265

Table III shows heteronuclear molecules with regular behavior. The valency in this group is generally two with the exception of CO molecule in which in accordance to COULSON's statement we found the valency to be three [7].

Table III

	k_e	r_e	$(e_1e_2)^{\frac{1}{2}}$	$\bar{D}_{ij}$	d
CO	19.02	1.128	2.96	70	0.286
CS	8.49	1.534	2.50	83	0.286
GeO	7.52	1.651	2.51	75	0.285
GeS	4.36	2.060	2.12	65.5	0.262
GeSe	3.78	2.190	2.08	57.5	0.262
SnO	5.62	1.838	2.51	64.5	0.256
SnS	3.54	2.260	2.12	49	0.269
SnTe	2.43	2.570	1.94	35.6	0.272
PbO	4.56	1.922	2.51	38	0.281

Table IV lists diatomic molecules containing atoms of IV/b and VII/b columns of the periodic system.

The uniformity is, — for the present purpose — satisfactory.

Table IV

	k_e	r_e	$(e_1e_2)^{\frac{1}{2}}$	D_{ij}	d
CCl	3.766	1.73	2.74	78.5	0.268
CI	2.171	2.18	2.50	57.4	0.259
SiF	4.890	1.60	2.68	88.0	0.311
SiCl	2.62	2.0	2.32	76.0	0.259
SiBr	2.21	2.14	2.23	69.0	0.256
GeF	3.925	1.67	2.68	92.0	0.256
GeCl	2.323	2.08	2.32	62.0	0.264
GeBr	1.971	2.29	2.24	56.0	0.269
SnCl	1.976	2.32	2.32	60.0	0.255

In Table V we can see that great difference exists between the molecules having element or elements belonging to the first periodic columns and between those having no such components. The *d* values of homonuclear alkali molecules or of alkali hydrides e.g., are more low than *d* values of other — more covalent — molecules belonging to IV—VII columns of the periodic system. The difference in behavior of values can be partly explained by the *s* and *p* character of bonds but the validity of (3) we find also restricted in the case of molecules containing *s*—*s* or *s*—*p* bonding. This difference in values of the *d* factors will be explained in what follows. The data of force constants, dissociation energies and interatomic distances are taken from the works of COTTRELL [6], HERZBERG [8], GAYDON [9], RICE and KLEMPERER [10], SUTTON [11], and PAULING [12].

As for the electronegativities we used data given by PAULING [13]. We tried to make calculations on the basis of electronegativities given by DAUDEL [14], but these results became worse, the strict parallelism between *s* and *p* character was lost.

Applying our equations for homonuclear molecules and a corresponding heteronuclear one we can write the following relationships

$$\bar{k}_i = d_i\, e_i\, \bar{D}_i^{1/2}\, r_i^{-1} \tag{4}$$

$$\bar{k}_j = d_j\, e_j\, \bar{D}_j^{1/2}\, r_j^{-1} \tag{5}$$

$$\bar{k}_{ij} = d_{ij}\, (e_i\, e_j)^{1/2}\, \bar{D}_{ij}^{1/2}\, r_{ij}^{-1} \tag{6}$$

Table V

	k_e	r_e	$(e_1e_2)^{\frac{1}{2}}$	D_{ij}	d_{ij}
H_2	5.734	0.742	2.1	104.2	0.199
Li_2	0.255	2.672	1.0	25	0.136
Na_2	0.172	3.078	0.9	17.3	0.141
K_2	0.099	3.923	0.8	11.8	0.140
Rb_2	0.082	4.20	0.8	10.8	0.131
Cs_2	0.069	4.42	0.7	10.4	0.135
F_2	4.453	1.435	4.0	36	0.266
Cl_2	3.279	1.988	3.0	57.1	0.287
Br_2	2.457	2.284	2.8	45,5	0.298
I_2	1.721	2.667	2.5	35.6	0.308
LiH	1.026	1.596	1.448	58	0.148
NaH	0.781	1.887	1.376	47	0.156
KH	0.561	2.244	1.296	43	0.148
RbH	0.545	2.376	1.296	39	0.160
CsH	0.467	2.494	1.212	42	0.148
LiCl	1.499	1.51	1.73	115	0.158
NaCl	1.100	2.361	1.64	98	0.161
KCl	0.865	2.667	1.55	101	0.148
RbCl	0.767	2.787	1.55	102	0.138
CsCl	0.720	2.906	1.45	101	0.141
FCl	4.483	1.628	3.46	60.5	0.271
FBr	4.095	1.756	3.35	55	0.289
BrH	4.117	1.414	2.43	85.5	0.260
ClH	5.157	1.275	2.51	102	0.259
IH	3.142	1.604	2.29	70.5	0.262

In case of covalency [3] is found to be correct. As a postulate of PAULING [12] we have

$$D_{ij} = (D_i D_j)^{1/2} + \Delta \tag{7}$$

where the D-s are the heats of formation and Δ is the resonance energy.

In covalent cases Δ has a low, sometimes negligible value.

Considering the covalent atomic radius rule:

$$r_{ij} = \frac{1}{2}(r_i + r_j) \tag{8}$$

or supposing that the difference between r_i and r_j is not too great:

$$r_{ij} = (r_i r_j)^{1/2} \tag{9}$$

and assuming Δ to be zero we can accept the following approximate relationship between the force constants

$$\bar{k}_{ij} = (\bar{k}_i \bar{k}_j)^{1/2} \tag{10}$$

Thus we can calculate force constants from each other in cases where (3) and (9) hold.

For dissociation energies including non covalent cases, remembering that $\bar{D}$-s are values reduced to unit valency

$$N_{ij} \bar{D}_{ij} = (N_i \bar{D}_i N_j \bar{D}_j)^{1/2} + \Delta \tag{11}$$

where N-s are representing valencies of the diatomic molecules.

Δ can also be divided by N_{ij} and then equals Δ', the value of resonance energy referred to unit valency

$$\frac{\Delta}{N_{ij}} = \Delta' \tag{12}$$

Actually, the N_{ij}-s are multiplying factors for restoring dissociation energy values taken for unit valency to the original ones of the complete molecule.

Putting all these relationships in proper order we obtain

$$\bar{k}_{ij} = (\bar{k}_i \bar{k}_j)^{1/2} \left(\frac{N_i N_j^{1/2}}{N_{ij}} \right)^{1/2} (1 + \Delta')^{1/2} \tag{13}$$

Although in some special cases *(e.g.* NO, BO, *etc.)* the interpretation of N_{ij} encounters some difficulties, nevertheless the equation, by using homonuclear data, yields force constants for heteronuclear molecules with a good approximation.

Based on the equations of fundamental importance we obtain another relationship:

$$\frac{\bar{k}_{ij}}{(\bar{k}_i \bar{k}_j)^{1/2}} = \frac{d_{ij}}{(d_i d_j)^{1/2}} \frac{\bar{D}_{ij}^{1/2} r_{ij}^{-1}}{(\bar{D}_i \bar{D}_j)^{1/2} (r_i r_j)^{-1}} \tag{14}$$

Introducing the notation

$$D_{ij}^{*} = \frac{\bar{D}_{ij}}{r_{ij}^2} \tag{15}$$

(14) will be modified as follows:

$$\frac{\bar{k}_{ij}}{(\bar{k}_i \bar{k}_j)^{1/2}} = \frac{d_{ij}}{(d_i\, d_j)^{1/2}} \left[\frac{D^*_{ij}}{(D^*_i\, D^*_j)^{1/2}}\right]^{1/2} \tag{16}$$

In the case of bonds of prevailingly covalent character, the value of $\frac{\bar{k}_{ij}}{(\bar{k}_i\, \bar{k}_j)^{1/2}}$ is nearly one, consequently:

$$\frac{\bar{k}_{ij}}{(\bar{k}_i\, \bar{k}_j)^{1/2}} = \left[\frac{D^*_{ij}}{(D^*_i\, D^*_j)^{1/2}}\right]^{1/2}$$

Table VI

	$\frac{\bar{k}_{ij}}{(\bar{k}_i\, \bar{k}_j)^{\frac{1}{2}}}$	$\left[\frac{D^*_{ij}}{(D^*_i\, D^*_j)^{\frac{1}{2}}}\right]^{\frac{1}{2}}$	$\bar{k}_{ii}$	$\bar{k}_{jj}$	$\bar{k}_{ij}$	$\bar{D}_{ii}$	$\bar{D}_{jj}$	$\bar{D}_{ij}$
NH	0.911	0.851	7.653	5.733	6.03	75	104.2	85
PH	1.000	0.970	1.852	5.733	3.26	39	104.2	87.5
CO	1.200	1.230	4.755	5.880	6.34	86	59	85
PN	0.895	0.893	1.852	7.653	3.39	39	75	46
SO	1.038	1.056	2.480	5.880	3.97	50.5	59	59.5
NO	0.952	0.948	7.653	5.880	6.38	75	59	60
CH	0.859	0.881	4.755	5.734	4.482	104.2	80	80
CS	1.235	1.151	4.755	2.480	4.244	85.5	50.5	82.5
IH	1.000	0.944	5.733	1.720	3.142	104.2	35.6	70.5
ClF	1.172	1.188	3.286	4.453	4.483	58	36.6	60.5
BrH	1.097	1.034	5.733	2.457	4.117	104.2	45.5	86.5

In Table VI we can see some results of calculations for molecules in which covalent character prevails.

The d_{ij} factors in simple polyatomic molecules. The d_{ij} factors possess characteristic features too if we survey also the bonds in simple polyatomic molecules where with a few exceptions we find *d* values between 0.23 and 0.25. The empirical data have been published by LADD and ORVILLE-THOMAS [15], HEATH and LINNETT [16] GOUBEAU et al. [17].

The numerical values can be found in Table VII.

We have carried out similar calculations in XH_3 type molecules belonging to the nitrogen column of the periodic system (X = N, P, As. *etc.*) The values of force constants and energy terms were taken from a paper of ALTI *et al.* [18] and

Table VII

Molecule	k_e	r_e	$(e_i e_j)^{\frac{1}{2}}$	$D_{ij}^{\frac{1}{2}}$	d_{ij}
BCl_3	3.64	1.74	2.45	10.45	0.248
BF_3	7.15	1.291	2.83	12.4	0.264
BBr_3	2.86	1.87	2.366	9.485	0.238
NF_3	4.91	1.37	3.46	8.065	0.241
$SbCl_3$	2.10	2.37	2.39	8.6	0.242
$AsCl_3$	2.14	2.161	2.45	8.37	0.226
PCl_3	2.17	2.043	2.51	8.8	0.201
$GeBr_4$	1.95	2.32	2.248	8.125	0.248
GeJ_4	1.523	2.48	2.12	7.14	0.249
$GeCl_4$	2.44	2.08	2.325	9.0	0.243
$SnCl_4$	2.30	2.30	2.325	8.72	0.261
$TiCl_4$	2.46	2.185	2.12	10.1	0.251
$SiCl_4$	2.58	2.02	2.325	9.54	0.235

from the monography of GAYDON, respectively. The resulting *d* values are given in Table VIII. As there is a remarkable agreement with the values expected on the basis of (10) we conclude that no interaction of too great influence can exist between the separate valence bonds. This assumption was supported by the fact that the valence force constants of XH_3 molecules agreed well with the square roots of the product of force constants for the hydrogen- and the diatomic X_2 molecule, respectively (within 1—2%). A possible reason for this agreement may be the fact that in the case of covalent bonds the Δ (resonance energy) values are only slightly different from zero. In Table VIII we compiled force constants resulting from normal coordinate analyses as well as from the harmonic oscillator approach for corresponding diatomic molecules together with *d* values evaluated by an analogous assumption.

Table VIII

Molecule	$\bar{k}_{ii}$	k_{jj}	$(\bar{k}_{ii} k_{jj})^{\frac{1}{2}}$	k_{ij}	d_{ij}
NH_3	7.653	5.733	6.621	6.954	0.278
PH_3	1.852	5.733	3.240	3.333	0.257
AsH_3	1.358	5.733	2.790	2.864	0.277
SbH_3	0.870	5.733	2.236	2.295	0.250

SUMMARY

The valence force constants of diatomic molecules depend on the electronegativity, bond distance and bond energy. In the large domain of molecules in which covalence prevails the proportionality factor is found to have a nearly constant value. The force constants of diatomic homo- and heteronuclear molecules can be calculated from each other. In cases, however, in which the ionic character cannot be neglected, a correction has to be applied by using the value of the ionic-covalent resonance energy. On this basis a relationship is found between the bond-strength and the force constants.

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ZUR BERECHNUNG DER GITTERENERGIEN DER ERDALKALIDICARBIDE CaC_2, SrC_2, BaC_2 UND DER DISSOZIATIONSENERGIE DES ACETYLIDIONS*

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Dissoziationsenergien von Molekülionen — beispielsweise die Dissoziationsenergie D des Acetylidions $C_2^{=}$, entsprechend der Gleichung

$$C_2^{=}(g) = 2\,C^{-}(g), \tag{1}$$

— können aus den Gitterenergien der Kristalle und experimentell zugänglichen thermodynamischen Daten mit Hilfe von Kreisprozessen berechnet werden.

Voraussetzung hierfür ist die Kenntnis eines verläßlichen Wertes für die Gitterenergie U_0, die nach M. BORN und J. E. MAYER [1] additiv durch Berechnung der einzelnen maßgeblichen Beiträge, nämlich der elektrostatischen Anziehungsenergie U_M, der Abstoßungsenergie U_R, der van der Waals-Energie U_D und der Nullpunktsenergie U_Z

$$U_0 = U_M - U_R + U_D - U_Z \tag{2}$$

erhalten werden kann.

1. Berechnung der elektrostatischen Anziehungsenergie U_M

Den Hauptbeitrag zur Gitterenergie liefert der elektrostatische Anziehungsterm U_M, die sogenannte Madelungenergie. Es ist daher wichtig, gerade diesen Anteil möglichst genau zu erfassen. Für komplexe Ionen (Molekülionen) ist jedoch die üblicherweise getroffene Annahme, daß das Ion durch eine punktförmige Ladung ersetzt werden kann, sicher nur eine sehr grobe Näherung. In früheren Arbeiten [2, 3] konnte gezeigt werden, daß man zu einer wesentlichen Verfeinerung gelangt, wenn man die reale Ladungsverteilung des Ions durch ein System von Punktladungen ersetzt und dessen Potential durch eine Multipolentwicklung darstellt.

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Die Madelungenergie wird üblicherweise in der Form

$$U_M = \frac{e_0^2 z^2 N_L}{a} M_a \tag{3}$$

geschrieben; worin

e_0 = Elementarladung,
z = kleinste im Gitter vorkommende Ionenwertigkeit,
N_L = Loschmidt-Zahl,
a = Gitterparameter und
M_a = Madelungkonstante, bezogen auf den Gitterparameter a bedeuten.

Nach der früher beschriebenen Methode [2] kann die Madelungkonstante M_a für die Gitter der Erdalkalidicarbide CaC_2, SrC_2 und BaC_2 (Raumgruppe D_{4h}^{17}) als Funktion des halben C—C-Abstandes d dargestellt werden. Man erhält für M_a folgenden Ausdruck:

$$M_a = A_0 + A_2 \left(\frac{d}{a}\right)^2 + A_4 \left(\frac{d}{a}\right)^4 + A_6 \left(\frac{d}{a}\right)^6 + \dots \tag{4}$$

$a = \frac{a'}{2}\sqrt{2}$; $a'/2$: kleinster Abstand der Schwerpunkte von Anion und Kation.

Die Koeffizienten A_0 bis A_6 für CaC_2, SrC_2 und BaC_2 sind in Tab. I angegeben. Da das Verhältnis $\left(\frac{d}{a}\right)$ für die betrachteten Verbindungen etwa 0,15 beträgt, genügt die Berücksichtigung weniger Glieder der Entwicklung. Für verschwindendes d geht der Ausdruck (4) in die Konstante A_0 über, die dem Wert der Madelungkonstante punktförmiger Ionen entspricht.

Tabelle I

*Koeffizienten zur Berechnung der Madelungkonstanten M_a für CaC_2, SrC_2 und BaC_2**

Substanz	a (Å)	c (Å)	d (Å)	c/a	A_0	A_2	A_4	A_6
CaC_2	3,875	6,37	0,5955	1,6438942	2,375800	−1,932934	13,19319	35,94263
SrC_2	4,108	6,68	0,5955	1,6259804	2,381052	−1,827774	13,82184	36,78469
BaC_2	4,398	7,06	0,5955	1,6052006	2,387522	−1,698049	14,59153	37,76199

* vgl. hierzu auch [2]

Um auch für andere Vertreter des CaC_2-Typs die Madelungkonstante rasch ermitteln zu können, wurden die Koeffizienten A_0, A_2, A_4 und A_6 für verschiedene Achsenverhältnisse, beginnend mit $\frac{c}{a} = \sqrt{2}$ (kubisch flächenzentriertes Gitter) in Abständen von $\sqrt{2}/100$ bis $\frac{c}{a} = 2{,}644579$ berechnet und in Tab. II zusammengestellt. Für Achsenverhältnisse, die in der Tab. 2 nicht enthalten sind, können die zugehörigen Koeffizienten durch Interpolation bestimmt werden, wofür sich beispielsweise die NEWTONsche Interpolationsformel [4] gut eignet.

2. Berechnung der van der Waals-Energie U_D und der Nullpunktsenergie U_Z

Für die van der Waals-Energie der Kristalle wurde näherungsweise nur der Dipol—Dipol-Beitrag

$$U_D = \frac{N_L}{a^6}\left\{S_6 c_{ij} + S_6' \frac{c_{ii} + c_{jj}}{2}\right\} = \frac{C}{a^6} N_L \tag{5}$$

berücksichtigt.

Die Gittersummen S_6 und S_6' wurden durch direkte Summation mit Hilfe einer elektronischen Rechenmaschine ermittelt. Die Koeffizienten c_{ij} sind nach F. LONDON [5, 6] gegeben durch

$$c_{ij} = \frac{3}{2} \frac{\varepsilon_i \varepsilon_j}{\varepsilon_i + \varepsilon_j} \alpha_i \alpha_j , \tag{6}$$

worin ε_i und ε_j charakteristische Energiewerte, α_i und α_j die Polarisierbarkeiten der Teilchen i und j bedeuten.

Eine andere Beziehung für die Wechselwirkungskonstante c_{ij} ist von J. C. SLATER und J. G. KIRKWOOD [7] abgeleitet worden

$$c_{ij} = \frac{3}{2} e_0^2 \sqrt{a_0} \frac{\alpha_i \alpha_j}{\sqrt{\frac{\alpha_i}{n_i}} + \sqrt{\frac{\alpha_j}{n_j}}} \tag{7}$$

a_0 = erster BOHRscher Radius,
n_i, n_j = effektive Anzahl der Elektronen in der äußersten Schale.

Die Polarisierbarkeit α kann bei Kenntnis des Brechungsindex n aus der Molrefraktion bestimmt werden.

Als einzigen Hinweis auf den Brechungsindex von CaC_2 (Modifikation I) findet man in der Literatur [8] die Angabe von $n > 1{,}75$. Um eine obere Schranke für n zu erhalten, wurde der Brechungsindex von CaC_2 (Modif. I) nach der Immersionsmethode bestimmt. Als Immersionsflüssigkeit wurde

Tabelle II

Koeffizienten zur Berechnung der Madelungkonstante M_a eines Gitters vom CaC_2-Typ für verschiedene Achsenverhältnisse c/a

c/a	A_0	A_2	A_4	A_6
1,414213	2,471432	0,000000	24,23462	46,50815
1,428355	2,463373	−0,164486	23,32696	45,87008
1,442497	2,455659	−0,321623	22,45575	45,23493
1,456639	2,448276	−0,471750	21,61932	44,60033
1,470782	2,441211	−0,615193	20,81613	43,96449
1,484924	2,434450	−0,752257	20,04470	43,32632
1,499066	2,427979	−0,883238	19,30366	42,68495
1,513208	2,421787	−1,008412	18,59170	42,03987
1,527350	2,415861	−1,128042	17,90761	41,39096
1,541492	2,410191	−1,242382	17,25021	40,73830
1,555634	2,404764	−1,351672	16,61841	40,08213
1,569777	2,399572	−1,456139	16,01117	39,42287
1,583919	2,394602	−1,556001	15,42750	38,76112
1,598061	2,389848	−1,651465	14,86646	38,09750
1,612203	2,385299	−1,742728	14,32714	37,43267
1,626345	2,380945	−1,829978	13,80871	36,76747
1,640487	2,376780	−1,913396	13,31033	36,10264
1,654629	2,372798	−1,993153	12,83123	35,43898
1,668772	2,368980	−2,069408	12,37067	34,77733
1,682914	2,365331	−2,142321	11,92794	34,11849
1,697056	2,361840	−2,212040	11,50234	33,46326
1,711198	2,358499	−2,278705	11,09323	32,81234
1,725340	2,355303	−2,342453	10,69997	32,16646
1,739482	2,352244	−2,403411	10,32198	31,52641
1,753624	2,349318	−2,461704	9,958654	30,89279
1,767766	2,346519	−2,517449	9,609455	30,26620
1,781909	2,343841	−2,570759	9,273845	29,64721
1,796051	2,341278	−2,621741	8,951302	29,03642
1,810193	2,338826	−2,670496	8,641349	28,43427
1,824335	2,336481	−2,717122	8,343503	27,84122
1,838477	2,334237	−2,761715	8,057302	27,25768
1,852619	2,332089	−2,804363	7,782308	26,68398
1,866761	2,330035	−2,845152	7,518095	26,12051
1,880904	2,328071	−2,884161	7,264269	25,56748
1,895046	2,326190	−2,921471	7,020420	25,02517
1,909188	2,324391	−2,957154	6,799679	24,49377

c/a	A_0	A_2	A_4	A_6
1,923330	2,322671	−2,991283	6,561183	23,97343
1,937472	2,321024	−3,023924	6,345073	23,46431
1,951614	2,319449	−3,055144	6,137523	22,96655
1,965756	2,317942	−3,085006	5,938197	22,48016
1,979898	2,316501	−3,113567	5,746788	22,00522
1,994041	2,315122	−3,140884	5,562981	21,54175
2,008183	2,313803	−3,167012	5,386498	21,08973
2,022325	2,312540	−3,192004	5,217057	20,64915
2,036467	2,311333	−3,215908	5,054380	20,21994
2,050609	2,310178	−3,238772	4,898210	19,80205
2,064751	2,309074	−3,260641	4,748303	19,39538
2,078893	2,308016	−3,281559	4,604407	18,99983
2,093036	2,307005	−3,301566	4,466295	18,61529
2,107178	2,306039	−3,314943	4,333737	18,24163
2,121320	2,305113	−3,339009	4,206525	17,87729
2,135462	2,304227	−3,356518	4,084448	17,52632
2,149604	2,303381	−3,373266	3,967301	17,18439
2,163746	2,302570	−3,389286	3,854897	16,85266
2,177888	2,301795	−3,404608	3,747051	16,53100
2,192031	2,301055	−3,419265	3,643578	16,21922
2,206173	2,300345	−3,433285	3,544312	15,91711
2,220315	2,299667	−3,446695	3,449084	15,62448
2,234457	2,299018	−3,459522	3,357737	15,34114
2,248599	2,298397	−3,471792	3,270115	15,06688
2,262741	2,297804	−3,483528	3,186073	14,80149
2,276883	2,297236	−3,494753	3,105464	14,54477
2,291025	2,296669	−3,505491	3,028160	14,29650
2,305168	2,296172	−3,515762	2,954024	14,05647
2,319310	2,295675	−3,525589	2,882930	13,82450
2,333452	2,295199	−3,534986	2,814756	13,60036
2,347594	2,294744	−3,543975	2,749388	13,38383
2,361736	2,294309	−3,552573	2,686709	13,17474
2,375878	2,293893	−3,560799	2,626616	12,97285
2,390020	2,293495	−3,568666	2,569003	12,77798
2,404163	2,293114	−3,576192	2,513767	12,58992
2,418305	2,292749	−3,583390	2,460820	12,40847
2,432447	2,292400	−3,590275	2,410060	12,23346
2,446589	2,292067	−3,596863	2,361406	12,06465
2,460731	2,291748	−3,603163	2,314768	11,90192

c/a	A_0	A_2	A_4	A_6
2,474873	2,291443	−3,609189	2,270066	11,74503
2,489015	2,291151	−3,614954	2,227221	11,59381
2,503158	2,290871	−3,620468	2,186160	11,44812
2,517300	2,290604	−3,625742	2,146805	11,30772
2,531442	2,290349	−3,630788	2,109091	11,17249
2,545584	2,290104	−3,635613	2,072951	11,04223
2,559726	2,289871	−3,640230	2,038318	10,91681
2,573868	2,289647	−3,644646	2,005130	10,79604
2,588010	2,289433	−3,648870	1,973331	10,67979
2,602152	2,289229	−3,652910	1,942863	10,56789
2,616295	2,289033	−3,656774	1,913669	10,46021
2,630437	2,288846	−3,660471	1,885699	10,35659
2,644579	2,288667	−3,664008	1,858902	10,25690

MERWINsche Lösung [9] verwendet, deren Brechungsindex ($n_D = 1{,}868$) durch Auflösen von $AsBr_3$, Sb_2S_3 und As_4S_4 noch erhöht werden konnte. Hierbei zeigte sich, daß die Zugabe von $AsBr_3$ zwar den Brechungsindex erniedrigt, jedoch eine größere Löslichkeit von Sb_2S_3 und As_4S_4 bewirkt, so daß auf diese Weise Flüssigkeiten mit einer Brechzahl bis zu $n = 1{,}94$ erhalten werden konnten. Da CaC_2 überaus hygroskopisch ist* und keine großen Kristallite der Modifikation I erhalten werden konnten, gestaltete sich die Bestimmung von n überaus schwierig. Selbst bei oftmaliger Wiederholung des Versuches konnten jedoch keine Kristalle mit einem höheren Brechungsindex als $n = 1{,}91$ gefunden werden, so daß dieser Wert als Maximalwert des Brechungsindex der Modifikation I angesehen werden kann.

Aus dem Brechungsindex von CaC_2 und der bekannten Polarisierbarkeit des Ca-Ions wurde die Elektronen-Polarisierbarkeit $\alpha_{C_2^=}$ des Acetylidions ermittelt (Tab. III).

Da das Acetylidion mit dem N_2-Molekül isoelektronisch ist, liegt die Annahme nahe, beiden Teilchen gleiche effektive Elektronenzahlen n_i zuzuschreiben, so daß nach (7) annähernd die Beziehung

$$\frac{c_{C_2^= - C_2^=}}{c_{N_2 - N_2}} = \left(\frac{\alpha_{C_2^=}}{\alpha_{N_2}}\right)^{3/2} \tag{8}$$

gilt.

---

* Alle Untersuchungen wurden in einem mit getrocknetem N_2 gespülten Hantierkasten vorgenommen.

Tabelle III

Van der Waals-Energien der Erdalkalidicarbide sowie zu deren Berechnung nötige Zwischenergebnisse

	CaC_2	SrC_2	BaC_2
α_{Kat} (10^{-24} cm^3)	1,1 10)	1,6 10)	2,5 10)
α_{An} (10^{-24} cm^3)	4,315	4,654	4,980
$\varepsilon_{\mathrm{Kat}}$ (10^{-11} erg)	1,322	1,769	2,069
$\varepsilon_{\mathrm{An}}$ (10^{-11} erg)	2,969	2,858	2,764
$c_{\mathrm{Kat-Kat}}$ (10^{-60} erg cm^6)	12 11)	34 11)	97 11)
$c_{\mathrm{An-An}}$ (10^{-60} erg cm^6)	414,6	464,4	514,1
$c_{\mathrm{Kat-An}}$ (10^{-60} erg cm^6)	65,14	122,1	221,0
C (10^{-60} erg cm^6)	629,9	991,9	1624
$S_{6,a}$	41,9998	42,5196	43,1695
$S'_{6,a}$	10,7968	11,0190	11,2881
U_D (kcal Mol^{-1})	21,42	23,75	25,83

Der Koeffizient $c_{N_2-N_2}$ wurde aus den von E. A. MASON und W. E. RICE [12] angegebenen Parametern für ein modifiziertes Buckingham (6-exp) Potential berechnet.

$$c_{N_2-N_2} = 108 \cdot 10^{-60} \text{ erg cm}^6,$$

$$\alpha_{N_2} = 17{,}6 \cdot 10^{-25} \text{ cm}^3.$$

Einsetzen von $c_{C_2^=-C_2^=}$ und $\alpha_{C_2^=}$ in (6) erlaubt die Ermittlung von von $\varepsilon_{C_2^=}$. In gleicher Weise kann mit Hilfe des Literaturwertes [11] von $c_{Ca^{2+}-Ca^{2+}}$ die charakteristische Energie $\varepsilon_{Ca^{2+}}$ erhalten werden. Die Kenntnis von $\varepsilon_{Ca^{2+}}$ und $\varepsilon_{C_2^=}$ gestattet nun $c_{Ca^{2+}-C_2^=}$ nach (6) zu berechnen.

Für die Berechnung der van der Waals-Energien von SrC_2 und BaC_2 wurde angenommen, daß sich die Werte für $c_{C_2^=-C_2^=}$ in der Reihe CaC_2, SrC_2 und BaC_2 in gleicher Weise ändern, wie die Koeffizienten $c_{\text{Anion-Anion}}$ der Erdalkalidioxide und -sulfide [11].

Tab. III. zeigt die van der Waals-Energien der Erdalkalidicarbide sowie die wichtigsten bei ihrer Berechnung auftretenden Zwischenergebnisse.

Die Nullpunktsenergie wurde nach der Gleichung

$$U_Z = \frac{9}{4} R\Theta \tag{9}$$

berechnet, wobei Θ die charakteristische Temperatur bedeutet. Der Wert von Θ für CaC_2 wurde aus Daten für die Molwärmen [14] bei tiefen Temperaturen ermittelt. Die Θ-Werte für SrC_2 und BaC_2 wurden in Anlehnung an die Verhältnisse bei den Erdalkalioxiden geschätzt. Die auf diese Weise erhaltenen Nullpunktsenergien sind in Tab. IV wiedergegeben.

Tabelle IV

Nullpunktsenergien von CaC_2, SrC_2 und BaC_2

Substanz	Θ (°K)	U_z (kcal/Mol)
CaC_2	300	1,3
SrC_2	230	1,0
BaC_2	200	0,9

3. Berechnung der Abstoßungsenergien

Für ein tetragonales Kristallgitter kann die Abstoßungsenergie in der Form

$$U_R = 4\, B_a \exp\left(-g\frac{a}{2}\sqrt{2}\right) + 2\, B_c \exp\left(-g\frac{c}{2}\right) \tag{10}$$

dargestellt werden. Da die Kompressibilitäten der Erdalkalidicarbide offenbar nicht bekannt sind, wurde für den Abstoßungsexponenten g der von M. L. HUGGINS und Y. SAKAMOTO [11] für die Erdalkalioxide und -sulfide gewählte Wert $g = 2{,}5$ (Å^{-1}) benützt. Diese Annahme wird durch die weitgehende Mischbarkeit von CaC_2 und CaS [15] nahegelegt, aus der auf ähnliche Abstoßungskräfte in diesen beiden Verbindungen geschlossen werden kann.

Um die Koeffizienten B_a und B_c zu bestimmen, bedient man sich der Gleichgewichtsbedingungen

$$\left(\frac{\partial U\,(a, c, d)}{\partial a}\right)_{\substack{c,\, d\\ a=a_0}} = 0 \tag{11}$$

und

$$\left(\frac{\partial U\,(a, c, d)}{\partial c}\right)_{\substack{a,\, d\\ c=c_0}} = 0\,. \tag{12}$$

Bei der Differentiation von $U\,(a, c, d)$ ist jedoch zu berücksichtigen, daß im vorliegenden Falle die Madelungkonstante eine Funktion von $\left(\frac{c}{a}\right)$ ist. Um diese Abhängigkeit analytisch darstellen zu können, wurden die Koeffizienten A_n

im Bereich von $1{,}57 < \frac{c}{a} < 1{,}70$ durch Ausgleichspolynome der Form $A_n = A_{n0} + A_{n4}\left(\frac{a}{c}\right)^4$ wiedergegeben (Tab. V). Die c-Abhängigkeit der in den van der Waals-Energien auftretenden Gittersummen S_6 und S'_6 wurde bei der Differentiation vernachlässigt.

Tabelle V

Koeffizienten zur Berechnung der Madelungkonstante M_a

nach: $M_a = \sum\limits_{\substack{n=0 \\ n \text{ gerade}}}^{n=6} \left\{A_{n0} + A_{n4}\left(\frac{a}{c}\right)^4\right\}\left(\frac{d}{a}\right)^n$

für $1{,}57 < c/a < 1{,}70$

n	A_{n0}	A_{n4}
0	2,25866	0,8555
2	−4,27913	17,138
4	−0,8124	102,233
6	17,339	135,119

$U\,(a, c, d)$ kann in folgender Form geschrieben werden:

$$U\,(a,c,d) = \frac{N_L z^2 e_0^2}{a} \sum_{\substack{n=0 \\ n \text{ gerade}}}^{n=6} \left\{A_{n0} + A_{n4}\left(\frac{a}{c}\right)^4\right\}\left(\frac{d}{a}\right)^n - $$
$$- 4B_a e^{-g\frac{a}{2}\sqrt{2}} - 2B_c e^{-g\frac{c}{2}} + \frac{C}{a^6} N_L - U_z\,. \tag{13}$$

Die Bedingungen (11) und (12) führen zu

$$B_a = \frac{\sqrt{2}}{4g\,e^{-g\frac{a}{2}\sqrt{2}}} \left\{\frac{6C}{a^7} N_L + \frac{N_L z^2 e_0^2}{a^2} \sum_{\substack{n=0 \\ n \text{ gerade}}}^{n=6} \left[(n+1)\,A_{n0} + \right.\right.$$
$$\left.\left. + (n-3)\,A_{n4}\left(\frac{a}{c}\right)^4\right]\left(\frac{d}{a}\right)^n\right\} \tag{14a}$$

und

$$B_c = \frac{4}{g\,e^{-g\frac{c}{2}}} \frac{N_L z^2 e_0^2}{a^2} \left(\frac{a}{c}\right)^5 \sum_{\substack{n=0 \\ n \text{ gerade}}}^{n=6} A_{n4}\left(\frac{d}{a}\right)^n . \tag{14b}$$

Nach Einsetzen von (14*a*, *b*) in (10) erhält man

$$U_R = \frac{\sqrt{2}}{2ga}\left\{6U_D + \frac{U_M}{M_a}\sum_{\substack{n=0\\ n\ \text{gerade}}}^{n=6}\left[(n+1)A_{n0} + (n-3)A_{n4}\left(\frac{a}{c}\right)^4\right]\left(\frac{d}{a}\right)^n + \right.$$

$$\left. + 4\sqrt{2}\,\frac{U_M}{M_a}\sum_{\substack{n=0\\ n\ \text{gerade}}}^{n=6} A_{n4}\left(\frac{d}{a}\right)^n\right\} \qquad (15)$$

Die auf diese Weise berechneten Abstoßungsenergien, die zweifellos mit einer größeren Unsicherheit behaftet sind als die anderen Energiebeiträge, sind in Tab. VI angegeben. In dieser Tabelle sind auch die Werte für die Gitterenergien zusammengestellt.

Tabelle VI

Gitterenergien von CaC_2, SrC_2 und BaC_2

Energiebeitrag	CaC_2	SrC_2	BaC_2
U_M (kcal/Mol)	800,95	759,05	712,77
U_D (kcal/Mol)	21,42	23,75	24,83
$-\ U_R$ (kcal/Mol)	−127,8	−117,7	−106,3
$-\ U_Z$ (kcal/Mol)	− 1,3	− 1,0	− 0,9
U (kcal/Mol)	693,3	664,1	630,4

4. Berechnung der Dissoziationsenergie *D* des Acetylidions

Rechnet man die Gitterenergie auf die Temperatur 298°K um und kombiniert man diesen Wert mit der Bildungswärme ΔH des Erdalkalidicarbids sowie mit der Ionisierungsenergie I und der Sublimationswärme S(Me) des Erdalkalimetalls in folgendem Kreisprozeß

$$\begin{tikzcd}
\text{Me (s)} + 2\text{C (Graphit)} \arrow[r, "\Delta H"] \arrow[dd, "\text{S (Me)}"'] \arrow[dr, "X"] & \text{MeC}_2\,\text{(s)} \\
 & \text{C}_2^{=}\,\text{(g)} - 2\text{e}^- \arrow[u, "-U_0 - \int_0^{298}[6R - C_p(s)]\,dT"'] \\
\text{Me (g)} \arrow[r, "\text{I}"] & \text{Me}^{2+}\,\text{(g)} + 2\text{e}^-
\end{tikzcd}$$

so erhält man

$$X = U_0 + \int_0^{298} [6\,R - C_p(s)]\ dT + \Delta H - S(Me) - I$$

die Bildungswärme X von $C_2^{=}$ (g) aus 2 C (Graphit) und 2 Elektronen. Die auf 298 °K bezogenen Enthalpiebeträge der einzelnen Schritte dieses Kreisprozesses sind in Tab. VII angeführt.

Tabelle VII

		Ca	Sr	Ba
U_{298}	(kcal/Mol)	695,7	666,3	632,6
S	(kcal/Mol)	42,2 [16]	39,1 [16]	41,7 [16]
I	(kcal/Mol)	414,8 [17]	385,7 [17]	350,9 [17]
Δ H	(kcal/Mol)	− 15,0 [18]	− 20,2 [19]	− 19,5 [19]
X	(kcal/Mol)	223,7	221,3	220,5

Aus einem weiteren Kreisprozeß, durch den die Bildungswärme X mit der Sublimationswärme von Graphit S(C) und der Elektronenaffinität $E(C^-)$ des C-Atoms verknüpft werden, kann die Dissoziationsenergie D des $C_2^{=}$-Ions in zwei C^--Ionen abgeleitet werden.

$$\begin{tikzcd}
\text{2 C (Graphit)} \arrow[r, "2S(C)"] & \text{2 C (g)} \\
+\,2e^- \arrow[d, "X"] & +\,2e^- \\
C_2^{=}\,(g) \arrow[r, "D"'] & 2C^-\,(g) \arrow[u, "2E(C)"']
\end{tikzcd}$$

Wählt man für X den sich aus den Erdalkalidicarbiden ergebenden Mittelwert X = 222 kcal/Mol, so erhält man mit S(C) = 170 kcal/Mol [18] und E(C) = 26 kcal/Mol[20] für die Dissoziationsenergie D = 66 kcal/Mol.

Wie aus dem betrachteten Beispiel zu ersehen ist, hat die vorgeschlagene Methodik zur Berechnung der Gitterenergien von Kristallen mit komplexen Ionen die Möglichkeit eröffnet, Dissoziationsenergien von Molekülionen zu berechnen und damit einen Einblick in deren Bindungsverhältnisse zu gewinnen.

ZUSAMMENFASSUNG

Die Gitterenergien von $CaC_2^=$, SrC_2 und BaC_2 werden unter Berücksichtigung der nicht sphärischen Ladungsverteilung des Acetylidions berechnet. Aus diesen Daten werden die Bildungswärme des $C_2^=$-Ions

2 C (Graphit) + 2 *e* = $C^=$ (g), X = 220 kcal/Mol

und die Dissoziationsenergie

$C_2^=$ (g) = 2 C^- (g) D = 66 kcal/Mol

ermittelt.

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ESTIMATION OF ENTROPY AND HEAT OF FORMATION OF FREE RADICALS, I.

STATISTICAL THERMODYNAMIC CALCULATION OF ENTROPIES

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Reliable knowledge of thermodynamic properties of radicals would facilitate the investigation of reactions proceeding via free radicals. However, heat of formation values from kinetic and electron impact sources are often rather doubtful. No self-consistent results are available even for the alkyl radicals. Entropies, apart from the simplest cases, are entirely lacking. Under these circumstances it is reasonable and desirable to consider the possibilities of estimating free radical properties. To begin with, entropies were calculated by statistical thermodynamic methods based on molecular data for certain simple free radicals of which not more than rough estimations are available in the literature.

Method of calculation

The calculation of entropies of simple polyatomic molecules has been worked out in detail (see *e.g.* [1], [2], [3], [4]). These methods can be applied to free radicals provided that data on structure, frequencies, barrier of internal rotations, *etc.* are available.

The basic equation for statistical entropy calculation is

$$S = k \ln \mathrm{W}. \tag{1}$$

W, *i.e.* thermodynamic multiplicity, can be approximately separated into a product of contributions due to different degrees of freedom. Therefore, entropy is separable into a sum of translational, rotational, etc. contributions:

$$S = S_{\mathrm{trans.}} + S_{\mathrm{rot.}} + S_{\mathrm{int.\,rot.}} + S_{\mathrm{vib.}} + S_{\mathrm{elec.}} + S_{\mathrm{n.\,s.}} \tag{2}$$

Neglecting the nuclear spin contribution and taking the electronic entropy equal to $R \ln 2$ (the contribution of the unpaired electron, assuming doublet ground state for the atom carrying this electron), the entropy becomes calculable by means of known formulae:

The SACKUR-Tetrode equation for the translational entropy is

$$S_{\text{trans.}} = R\left(\frac{3}{2}\ln M + \frac{5}{2}\ln T - \ln P\right) - 2.298 \tag{3}$$

where R, M, T and P denote the gas constant (in cal/mol. degree), the molecular weight (in grams), the temperature (in °K) and the gas pressure (in atmospheres) respectively.

Treating each vibrational degree of freedom, in a first approximation, as a simple harmonic-oscillator, the vibrational entropy is given by the expression

$$S_{\text{vib.}} = R\sum_i\left[\frac{x_i}{e^{x_i}-1} - \ln\left(1-e^{-x_i}\right)\right] \tag{4}$$

in which x_i depends on the wave number, $\bar{\nu}_i$, of the i-th fundamental frequency (expressed in cm^{-1}):

$$x_i = \frac{1.4384\,\bar{\nu}_i}{T} \tag{5}$$

Equation (6) gives the rotational entropy for a nonlinear polyatomic system treated as a rigid rotator. I_x, I_y and I_z denote the principial moments of inertia (in g-mole. Å^2), while σ designates the external symmetry number. The latter is defined as the number of indistinguishable positions into which the molecule or radical can be turned by simple rigid rotations.

$$S_{\text{rot.}} = R\left[\frac{3}{2}\ln T + \frac{1}{2}\ln\left(I_x I_y I_z\right) - \ln\sigma\right] - 5.38 \tag{6}$$

The principal moments of inertia were estimated by HIRSCHFELDER's method [5].

Entropy contributions of free internal rotations can be expressed by means of the adequate partition functions:

$$S_{\text{int. rot., free}} = R\left(\frac{1}{2} + \ln Q_{\text{int. rot., free}}\right) \qquad (7$$

The partition function for free rotation of a group with respect to the radica as a whole is:

$$Q_{\text{int. rot., free}} = \frac{\left(8\pi^3 I_{\text{red}}\, kT\right)^{1/2}}{hn} \tag{8}$$

where n is the symmetry number of the internal rotation and I_{red} the "reduced" moment of inertia. (Concerning the calculation of the latter see *e.g.* [4].) Contribution of restricted internal rotation was calculated from the partition function of free rotation and the energy barrier hindering free rotation with the aid of PITZER's tables [6].

Assumptions employed in the calculations. Structure, bond distances and symmetry number

Identical assumptions were made for radicals belonging to a certain structural type. Explanations for these assumptions are given below. Classification into types was to some extent arbitrary and was based exclusively upon practical viewpoints.

a) *$\dot{C}H_3$ type.* Assumption: Planar configuration with bond angles of 120° for methyl, and isoelectronic deuterated methyl radicals.

Planar configuration has been found the energetically most favourable one for the methyl radical [7]. Analysis of the absorption spectra of $\dot{C}H_3$ (and $\dot{C}D_3$) radicals led HERZBERG to the same conclusion [8]. Deviation from planarity, Θ (the angle between the principal symmetry axis and the bond direction), does certainly not exceed 10°. On the basis of the C^{13} hyperfine splitting $\Theta < 5°$ has been suggested [9]. (Concerning proton hyperfine splitting and conclusions drawn of it see [10]).

b) *$\dot{C}H_2R$, $\dot{C}HR_2$ and $\dot{C}R_3$ types,* where R denotes alkyl, substituted alkyl or unsaturated hydrocarbon groups. Assumption: Planar or "effectively" planar configuration for the environment of the central (unpaired electron carrying) carbon atom; bond angles 120°.

In Walsh's opinion, molecules, radicals or ions characterized by the general formula H_2AB, furthermore AB_3 (and B_2AC), should have planar configuration if the number of valency electrons is ≤ 12 and ≤ 24, resp. [11]. Likewise, planar configuration is expected in the environment of the central C-atom of primary and secondary alkyl radicals.

According to BENSON, the structure surrounding the trivalent carbon atom in the CHJ_2CHJ radical is planar [12]. It is only this configuration that satisfies the symmetry requirements resulting from the principle of microscopic reversibility, and renders possible the explanation of the high exchange/isomerization ratio (found in the system consisting of iodine and *cis*-1,2-diiodoethylene). Regarding the planarity of certain fluorinated radicals belonging to the discussed types, see references [13] and [14].

Direct experimental verification of the configuration of the $\dot{C}RR'R''$ (or $\dot{C}HRR'$) radical may be carried out by optical activity measurements. It has been shown [15] for instance that the CRR'R" group of the molecule CHRR'R" does not preserve pyramidal structure when converted into the free radical, since chlorination results in racemic product.

For certain radicals, belonging to the discussed types, non-planarity in the environment of the central carbon atom may be a result of bulky substituents or of the presence of interacting highly polar groups [16].

c) *$\dot{C}H_2X$ and $CH_3\dot{C}HY$ types,* where X = OH, CH_3O or NH_2 and Y = halogen or OH. Assumption: By reason of the relationship with the types discussed under *b)*, planar arrangement and bond angles of 120° were presumed for the environment of the central atom.

d) *$\dot{C}H_2(Hlg)$, $\dot{C}H(Hlg)_2$ and $\dot{C}(Hlg)_3$ types.* Assumption: Pyramidal structure and bond angles decreasing in the following order: $\dot{C}H_2(Hlg)$, $\dot{C}H(Hlg)_2$, $\dot{C}(Hlg)_3$. The symmetry numbers and Θ values used in the calculations were $\Theta = 0°$ and $\sigma = 1$ for monohalides, $\Theta = 10°$ and $\sigma = 1$ for dihalides, $\Theta = 19.5°$ and $\sigma = 3$ for trihalides. (Θ is a measure of deviation from planarity. The symmetry axis of the hypothetical pyramid described by the three bonds arbitrarily regarded as equal, forms an angle with any bond which is the complementary angle of Θ. In case of the $\dot{C}Cl_3$ radical for instance Θ is directly equal to the angle between the C—Cl bond and the plane perpendicular to the symmetry axis.)

According to WALSH [11] particles of the formulae H_2AB and AB_3 have planar shapes if the number of valency electrons is ≤ 12 and ≤ 24, respectively. If this is so, the $\dot{C}H_2(Hlg)$ and $\dot{C}(Hlg)_3$ radicals, having 13 and 25 valency electrons, should have pyramidal shapes.

On the basis of the isotope fluorine hyperfine splitting (E. S. R. spectrum) Θ values of 17.8 and 12.7° have been suggested for $\dot{C}F_3$ and $\dot{C}HF_2$, respectively [14]. The $\dot{C}H_2F$ radical is nearly planar; $\Theta < 5°$. Deviation from planarity in other halomethyl radicals should be similar to the fluoromethyls. The lower electronegativity, decreasing the *s* character of the unpaired electron, and the higher steric hindrance exerted by the substituents in the other halogenated radicals, result in structures similar to those of the fluoromethyl radicals.

e) *$> C = \dot{C}R$ and $O = \dot{C}R$ types,* where R denotes a hydrogen atom or an alkyl group. Assumption: On the basis of known structures for formyl and vinyl radicals, bond angles of the central atom of the discussed types may be approximated by generalized C=C—R and O = C—R angles.

Contrary to the "π-electron radicals", the unpaired electrons in formyl and vinyl occupy — to the 0-th approximation — *sp* hybrid σ orbitals. (Such radicals are called "σ-electron radicals".)The exceptionally large isotope proton hyperfine splitting of formyl [17] and the ESR spectrum of vinyl radical [18] strongly support this supposition.

According to the interpretation of the absorption spectrum, the valency angle in formyl radical is appr. 120° [19] (see furthermore [20]).

Comparison of the theoretically expected value with the experimental α-proton hyperfine splitting shows the bond angle of vinyl radical to be between 140° and 150° [18].

f) *$>C{=}CR{-}\dot{C}R_2$ type,* where R may denote a hydrogen atom or an alkyl group. Assumption: The environment of the central carbon atom is planar with bond angles of 120°.

The assumption seems to be justified on theoretical grounds [21]. The planar arrangement is a consequence of the endeavour of the system towards energy minimum. The unpaired electron is one of σ-type in the parent molecule and is converted into a π-type electron in the radical acquiring mobile character.

g) *$R\dot{O}$ type,* where R signifies an alkyl, $HC\overset{O}{/\!\!/}$ or $R'C\overset{O}{/\!\!/}$ group. Assumption: The structure of these radicals may be considered identical with the adequate parent molecules of which the radicals are formally derived by the loss of an hydrogen atom. It is not likely that the removal of this atom should bring about a significant change of the original structure.

h) *$\dot{N}R_2$ type,* where R stands for hydrogen atom or alkyl group. Assumption: Structures of the NR_2 group in the $\dot{N}R_2$ radical and the HNR_2 molecule are nearly the same.

Uniform bond length and bound angle values [3], [4] were used throughout except for the environment of the atom formally carrying the unpaired electron. From type to type, different approximations — discussed above — were applied to estimate the bond angles of the central atom. For the rest of the radicals the structure was supposed to be the same as in the parent molecule. A symmetry number directly derivable from the assumed structure was used.

Vibrational frequencies and potential barriers hindering internal rotation

Frequencies of the radical R were derived from the fundamental frequencies of the parent molecule RH by omitting three of them [22]. Relying on the frequency assignments given in the literature (or lacking such assignments depending on comparisons with generalized bond frequencies), the following three frequencies were omitted: *a)* for the type $-\dot{C}H_2$, 1 CH_3 stretching and 2 deformation frequencies; *b)* for the $>\dot{C}H$ and $=\dot{C}H$ types 1 CH_2 stretching and 2 CH_2 deformation frequencies; *c)* for $-\!\!>\dot{C}$ and $\geq\dot{C}$ types 1 CH stretching and 2 CH deformation frequencies; *d)* for the $-\dot{N}H$ type 1 NH_2 stretching and 2 NH_2 deformation frequencies; *e)* for the $-\dot{O}$ type 1 OH stretching, and 1 OH torsion frequency.

In general, the potential barrier hindering internal rotation in free radicals had to be taken as large as in the parent molecule [4], [23]. In some cases other models than the parent molecules had to be relied on. Small corrections (10% reduction of the potential barrier) were made in the cases where one of the atoms connected by the rotation axis carried the unpaired electron.

No calculation was made for entropy contribution of internal rotation about a certain bond in "conjugated radicals" (derivable from unsaturated molecules by the removal of a hydrogen atom from the α-position to the double bond). High potential barrier prevents this "internal rotation" as a consequence of electron delocalization. Contribution of torsion oscillation was calculated for this degree of freedom. The appropriate values of both butadiene and propene, butene-1, butene-2 served to estimate the frequency to be ~ 310 cm^{-1}. In a similar case EGGER and BENSON [24] estimate an entropy loss of 2.3 e. u. owing to the stiffening effect of the allylic resonance energy (cf. [27]).

Discussion of the results

The calculations were performed for 298°K, the results given in Tables I—VI refer to the ideal gas state and 1 atm. pressure. Beside part-results (translational, vibrational, *etc.* entropies), the principal moments of inertia are also included in the Tables. The errors — apart from certain exceptional cases (see below) — do not exceed ± 0.5 e.u., despite the numerous approximations which had to be used. Provided the assumed symmetry number is correct, the greatest error arises from the uncertainty in bond angles of the atom carrying the unpaired electron and from the uncertainty of the energy barrier values hindering internal rotation.

Inaccuracies of bond angles influence the rotational entropy value. The error is greatest for relatively simple radicals. As examples we discuss the halomethyl radicals where the angles vary within wide limits.

It has been established with sufficient certainty that the shapes of halomethyl radicals are pyramidal. Whereas monohalide radicals hardly deviate from planarity, bond angles of trihalomethyl radicals approach the tetrahedric limiting value; the dihalide radicals occupy intermediate position. Accordingly, different structures were assumed for the $\dot{C}H_2(Hlg)$ ($\sigma = 1, \Theta = 0°, \sphericalangle = 120°$), the $\dot{C}H(Hlg)_2$ ($\sigma = 1, \Theta = 10°, \sphericalangle = 117°$) and for the $\dot{C}(Hlg)_3$ ($\sigma = 3, \Theta = 19.5°, \sphericalangle = 109.5°$) radicals. In Table VII, calculated rotational entropies based on the aforesaid structures are compared with those corresponding to the planar ($\Theta = 0°$) and the tetrahedral ($\Theta = 19.5°$) extreme cases. The correct values lie necessarily between ($S_{\text{rot., tetrahedral}}$) and ($S_{\text{rot., planar}} + R \ln 2$) provided that the radicals are not strictly planar. Consequently, according to Table VII it follows that the error of the calculated rotational entropies is roughly 0.5 e.u.

An uncertainty of 1000 cal/mol in the estimation of the energy barrier hindering internal rotation may introduce — under the circumstances discussed — an error of appr. 0.5 e. u. The energy barrier of a certain internal rotation in a radical and its parent molecule may hardly differ significantly if

Table I

Calculated entropies of monosubstituted methyl radicals

Radical	$10^{39}\cdot I_1$ (g.cm^2)	$10^{39}\cdot I_2$ (g.cm^2)	$10^{39}\cdot I_3$ (g.cm^2)	$S_{trans.}$	$S_{rot.}$	$S_{int.\ rot.}$	$S_{vib.}$	S_{total}	$S(RH)^*$
$\dot{C}H_2D$	0.287	0.480	0.768	34.26	13.34	—	0.11	49.11	50.27
$\dot{C}H_2F$	0.287	3.141	3.429	36.42	18.06	—	0.18	56.04	56.86
$\dot{C}H_2Cl$	0.287	5.713	6.006	37.69	19.22	—	0.47	58.76	59.53
$\dot{C}H_2Br$	0.287	7.904	8.191	39.53	19.85	—	0.69	61.45	62.30
$\dot{C}H_2J$	0.287	10.021	10.308	40.74	20.32	—	0.91	63.35	64.03
$\dot{C}H_2CH_2Cl$	2.485	13.923	15.903	38.37	23.21	2.55	2.00	67.51	68.08
$\dot{C}H_2CH_2Br$	2.610	19.960	22.068	39.95	23.95	2.41	1.27	68.95	70.88
$\dot{C}H_2CH_2J$	2.702	25.128	27.329	41.02	24.42	2.30	2.87	71.99	71.88
$\dot{C}H_2OH$	0.394	0.544	1.181	36.23	15.58	1.80	0.22	55.21	59.47
$\dot{C}H_2CH_2OH$	2.359	8.080	9.935	37.34	22.15	4.33	1.33	66.54	69.57
$\dot{C}H_2OCH_3$	2.150	7.910	9.558	37.34	22.00	4.84	1.34	66.91	67.29
$\dot{C}H_2\overset{\overset{O}{\|}}{C}CH_3$	8.021	9.784	17.010	38.05	24.10	6.59	2.89	73.01	74.02
$\dot{C}H_2\overset{\overset{O}{\|}}{C}OH$	7.796	8.731	16.525	38.15	23.92	5.45	1.86	70.76	69.69
$\dot{C}H_2NH_2$	0.568	3.448	3.577	36.13	18.86	2.40	0.43	59.21	59.92

(For the meaning of S(RH)* see the text.)

Table II

Calculated entropies of disubstituted methyl radicals

Radical	$10^{39}\cdot I_1$ (g.cm^2)	$10^{39}\cdot I_2$ (g.cm^2)	$10^{39}\cdot I_3$ (g.cm^2)	$S_{trans.}$	$S_{rot.}$	$S_{int.rot.}$	$S_{vib.}$	S_{total}	$S(RH)^*$
$\dot{C}HD_2$	0.378	0.596	0.974	34.45	14.07	—	0.18	50.07	
$\dot{C}HF_2$	$I_1I_2I_3 = 121\cdot10^{-117}$			37.71	21.71	—	0.79	61.59	61.55
$\dot{C}HCl_2$	$I_1I_2I_3 = 1486\cdot10^{-117}$			39.20	24.20	—	2.27	67.05	67.33
$\dot{C}HBr_2$	$I_1I_2I_3 = 12619\cdot10^{-117}$			41.35	26.33	—	3.52	72.58	72.84
$\dot{C}HJ_2$	$I_1I_2I_3 = 101994\cdot10^{-117}$			42.64	28.40	—	4.23	76.65	79.60
$CH_3\dot{C}HCl$	2.966	8.969	11.437	38.37	22.63	2.38	1.86	66.61	67.28
$CH_3\dot{C}HBr$	2.090	22.807	24.422	39.95	23.96	2.20	1.20	68.69	70.08
$CH_3\dot{C}HJ$	2.178	28.484	30.188	41.02	24.43	2.00	2.87	71.70	71.61
$CH_3\dot{C}HOH$	1.941	9.542	10.916	37.34	22.22	4.19	1.38	66.51	68.77

(For the meaning of S(RH)* see the text.)

Table III

Calculated entropies of trisubstituted methyl radicals

Radical	$10^{39}\cdot I_1$ (g.cm^2)	$10^{39}\cdot I_2$ (g.cm^2)	$10^{39}\cdot I_3$ (g.cm^2)	$S_{trans.}$	$S_{rot.}$	$S_{int.rot.}$	$S_{vib.}$	S_{total}	*S(RH)**
$\dot{C}D_3$	0.596	0.596	1.191	34.62	12.53	—	0.25	48.77	51.50
$\dot{C}F_3$	8.814	9.125	17.630	38.61	21.97	—	1.74	63.71	63.41
$\dot{C}Cl_3$	24.396	25.269	48.609	40.15	25.00	—	5.67	72.20	72.24
$\dot{C}Br_3$	64.017	66.337	129.034	42.47	27.89	—	8.48	80.22	80.42

(For the meaning of S(RH)* see the text.)

Table IV

Calculated entropies of unsaturated hydrocarbon radicals

Radical	$10^{39}\cdot I_1$ (g.cm^2)	$10^{39}\cdot I_2$ (g.cm^2)	$10^{39}\cdot I_3$ (g.cm^2)	$S_{trans.}$	$S_{rot.}$	$S_{int\ rot.}$	$S_{vib.}$	S_{total}	*S(RH)**
$\dot{C}H_2CH_2CH : CH_2$	2.714	19.354	21.567	37.94	23.93	7.50	3.80	74.56	75.66
$\dot{C}H : CHCH_3$	1.795	8.290	9.679	36.75	21.88	2.40	1.95	64.36	65.18
$\dot{C}H : CHCH_2CH_3$	2.732	20.077	21.767	37.94	24.03	7.22	3.84	74.40	74.86
$CH_3\dot{C} : CH_2$	1.396	9.199	10.088	36.75	21.78	2.52	1.85	64.27	65.18
$CH_3CH_2\dot{C} : CH_2$	2.630	20.726	21.855	37.94	23.98	7.83	3.71	74.84	74.86
$CH_3\dot{C} : CHCH_3$**	2.062	23.860	24.756	37.94	24.00	5.76	4.57	73.65	73.62
$\dot{C}H_2CH : CH_2$	1.769	8.480	10.236	36.75	24.23	—	3.33	65.69	67.36
$\dot{C}H_2CH : CHCH_3$**	2.240	22.749	24.250	37.94	24.02	2.82	6.00	72.16	75.80
$CH_3\dot{C}HCH : CH_2$	2.613	20.409	22.504	37.94	23.99	1.96	5.16	70.43	74.86

(For the meaning of S(RH)* see the text. **trans isomer.)

Table V

Calculated entropies of alkoxyl radicals

Radical	$10^{39}\cdot I_1$ (g.cm^2)	$10^{39}\cdot I_2$ (g.cm^2)	$10^{39}\cdot I_3$ (g.cm^2)	$S_{trans.}$	$S_{rot.}$	$S_{int.\ rot.}$	$S_{vib.}$	S_{total}	*S(RH)**
$\dot{O}CH_3$	0.511	3.830	3.830	36.23	16.77	—	0.38	54.75	58.67
$\dot{O}CH_2CH_3$	2.327	8.395	9.693	37.34	22.15	2.04	1.26	64.18	68.77
$\dot{O}CH_2CH_2CH_3$	3.353	20.891	22.112	38.15	24.24	6.80	2.88	73.45	77.13
$\dot{O}CH(CH_3)_2$	9.609	9.902	17.011	38.15	24.29	4.00	3.68	71.50	72.98
$\dot{O}C(CH_3)_3$	17.310	17.310	18.604	38.79	23.33	5.94	5.85	75.28	78.88

(For the meaning of S(RH)* see the text.)

Table VI

Calculated entropies of miscellaneous free radicals

Radical	$10^{39}\cdot I_1$ (g.cm²)	$10^{39}\cdot I_2$ (g.cm²)	$10^{39}\cdot I_3$ (g.cm²)	$S_{trans.}$	$S_{rot.}$	$S_{int.rot.}$	$S_{vib.}$	$S_{total,}$	$S(RH)^*$
$.\overset{\overset{O}{\|}}{C}OH$	0.752	7.625	8.396	37.34	20.80	2.75	2.29	64.56	61.51
$H\overset{\overset{O}{\|}}{\dot{C}}$	$I_1I_2I_3 = 93\cdot10^{-117}$			37.34	21.45	—	0.47	60.64	61.50
$CH_3\overset{\overset{O}{\|}}{\dot{C}}$	8.745	8.947	16.191	38.15	24.04	2.30	1.85	67.72	68.89
$.\overset{\overset{O}{\|}}{C}Cl$	$I_1I_2I_3 = 35\cdot10^{-117}$			38.36	20.47	—	1.00	61.21	
$.\overset{\overset{O}{\|}}{C}Br$	$I_1I_2I_3 = 325\cdot10^{-117}$			39.95	22.69	—	1.43	65.44	
$\dot{N}HCH_3$	0.657	3.320	3.439	36.13	18.93	1.50	0.44	58.39	59.12

(For the meaning of S(RH)* see the text.)

the unpaired electron carrying group is remote from the rotation axis. Further, it is not to be expected generally that the difference in height of barriers should exceed 1000 cal/mol even if the unpaired electron is localized at one of the neighbouring groups rotating in opposite direction. Errors larger than 0.5 e. u. may only occur in the few cases where rotation of groups with two skeletal atoms had to be considered or the contributions of OH rotators were calculated. So far no satisfactory theoretical treatment has been given for the former, and energy barrier data are uncertain for the latter. (Though a reasonable solution of the problem of internal rotation in alcohols has been suggested recently; among others see [25].)

Finally, the accuracy of the torsion oscillation data of conjugated radicals should be considered. Unfortunately, there are no appropriate data available in the literature to make comparisons.

In Tables I—VI calculated total entropies (in the columns but last) can be compared with certain estimations (last columns headed by $S(RH)^*$) based on parent molecule entropy values. Estimating $S(RH)^*$, entropies of the parent molecules were corrected for symmetry number differences as well as for electron entropy contributions:

$$S(RH)^* = S(RH) - R\ln\frac{s_{\dot{R}}}{s_{RH}} + R\ln 2\,. \tag{9}$$

Table VII

Rotational entropies of halomethyl radicals calculated according to various assumptions

Structure	Radical	$\dot{C}H_2F$	$\dot{C}H_2Cl$	$\dot{C}H_2Br$	$\dot{C}H_2J$	$\dot{C}HF_2$	$\dot{C}HCl_2$	$\dot{C}HBr_2$	$\dot{C}HJ_2$	$\dot{C}F_3$	$\dot{C}Cl_3$	$\dot{C}Br_3$	$\dot{C}J_3$
Planar	$\Theta = 0°$, $\sigma = 2$	16.68	17.84	18.47	18.94	20.60	22.41	23.71	25.91				
	$\Theta = 0°$, $\sigma = 6$									20.90	23.88	26.84	
Assumed	$\Theta = 0°$, $\sigma = 1$	18.06	19.22	19.85	20.32								
	$\Theta = 10°$, $\sigma = 1$					21.71	24.20	26.33	28.40				
	$\Theta = 19.5°$, $\sigma = 3$									21.97	25.00	27.89	
Tetrahedral	$\Theta = 19.5°$, $\sigma = 1$	18.08	19.24	19.88	20.35	21.67	24.12	26.21	28.11				
	$\Theta = 19.5°$, $\sigma = 3$									21.97	25.00	27.89	

Comparison shows that estimation in this way is not more than a rough approximation for the entropies of free radicals. Due to the oversimplifications (neglecting differences in contributions of the degrees of freedom of molecules and radicals) this method of estimation gives too high entropies. Deviations from the calculated values usually exceed many times the limits of error of the latter. Estimations could be improved somewhat by setting out from molecules structurally more similar to the radical, as suggested by TROTMAN-DICKENSON [26].

SUMMARY

Entropies have been calculated by statistical thermodynamic methods for certain simple free radicals of different types. Calculations are based on molecular data, reasonable assumptions having been adapted concerning the structural differences of a radical and its parent molecule. The accuracy of calculated entropies is discussed. Finally, some remarks are made on an estimation method based on molecular entropies.

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THE BILLES POTENTIAL OF MOLECULAR VIBRATIONS

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I. Introduction

Recently **Billes** [1] has considered the secular equation in the theory of harmonic molecular vibrations [2] and published in this journal a solution with very interesting aspects. He claims to derive an exact and unique solution for all F matrix elements from frequency data alone, in addition to the G matrix elements. This feature is at once hard to accept in view of the well-established facts about insufficiency of the frequencies for calculating the force constants without approximations or additional data. One is tempted to seek for a mistake in **Billes**' argument, which needs some clarification. It is the aim of this work to provide an adequate explanation, and to give a further discussion of the **Billes** method. We have therefore introduced the term "Billes potential". We wish, however, to point out that virtually the same method has independently been derived by **Joseph Babu** in an unpublished work [3].

It is apparently wrong to consider the Billes method (see below) as an exact and unique calculation of force constants. The origin of this view seems to be the erroneous assumption that the transformation matrix (in our notation V), which diagonalizes the G matrix, *necessarily* also diagonalizes the F matrix. However, in spite of this mistake, the Billes method makes it possible to find a certain F matrix which exactly fits a known set of frequencies, and we find it to represent an interesting basis of approximate calculations of force constants.

II. Similarity transformations of G and F

A coordinate transformation $S = VS_v$, where S and S_v each represents a complete and independent set of coordinates, is associated with the following transformations of the corresponding G and F matrices:

$$G_v = V^{-1} G (V^{-1})' , \qquad F_v = V' F V ,$$

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* A part of this work was made at the *Department of Chemistry, Oregon State University, Corvallis, Oregon* (USA), and supported by the *National Science Foundation.*

Both relations will simultaneously become similarity transformations when V is an orthogonal matrix. Now let V designate an orthogonal matrix which diagonalizes G, *viz.*

$$V^{-1}\, G\, V = \Gamma. \tag{1}$$

Such a transformation matrix will always be obtainable uniquely (apart from some trivial signs), since G is symmetric. In the Billes potential one assumes that V simultaneously diagonalizes the F matrix, *i.e.*:

$$V^{-1}\, F\, V = \Phi \tag{2}$$

where Φ is a diagonal matrix.

III. Theoretical discussion of the Billes potential

1. The assumption of the Billes potential implies the postulation of a coordinate set S_v, in which both G and F (*i.e.* Γ and Φ) are diagonal, and which is connected to the original set of internal coordinates by an orthogonal transformation:

$$S = V\, S_v \tag{3}$$

In normal coordinates (Q) the G and F matrices (*i.e.*, the identity matrix E, Λ) are no doubt diagonal, but the transformation

$$S = L\, Q \tag{4}$$

is *not* orthogonal in general.

2. Combining (1) and (2) gives:

$$V^{-1}\, G\, F\, V = \Gamma\Phi. \tag{5}$$

Since

$$L^{-1}\, G\, F\, L = \Lambda, \tag{6}$$

it appears that

$$L = V\, d \tag{7}$$

where d is a diagonal matrix. In fact, the Billes potential may be defined assuming that the L matrix may be "normalized" (*i.e.* multiplied by a diagonal matrix) to an orthogonal matrix. The d matrix of Eq. (7) is connected with Γ of Eq. (1) through

$$d\, d' = d^2 = \Gamma. \tag{8}$$

3. Since obviously

$$\Gamma\Phi = \Phi\Gamma, \tag{9}$$

it appears as a consequence of the assumption of the Billes potential that G and F must commute, *i.e.,*

$$G\ F = F\ G. \tag{10}$$

IV. Determination of the Billes potential

For the sake of completeness we repeat here the procedure of determining the Billes potential, as published by BILLES [1].

First the characteristic values of G *(viz.* γ_i*)* and the normalized characteristic vectors (given as the orthogonal V matrix) are determined (cf. Eq. 1). Next the diagonal Φ matrix is found according to

$$\Lambda = \Gamma\Phi, \qquad \varphi_i = \lambda_i/\gamma_i \tag{11}$$

where $\lambda_i (= 4\ \pi^2\ c^2\ \omega_i^2)$, γ_i and φ_i designate the diagonal elements of the appropriate matrices. Finally the F matrix is determined according to

$$F = V \Phi\ V'. \tag{12}$$

It should be emphasized that the characteristic values γ_i $(i = 1, 2, \ldots, n)$ may be arranged in $n!$ ways for a given sequence of the λ's. In this way $n!$ solutions are obtained for the force constants, of which not more than one set may have physical significance. The same sort of ambiguity is encountered by determination of the force field by other methods.

It is a very interesting aspect of the BILLES potential that the method allows to select one of the solutions in a systematic manner. It seems namely to be reasonable to arrange the characteristic values γ_i according to their magnitudes in the same sequence as the λ's, for instance both in the sequence of falling magnitudes.

V. Conclusions

The utility of the BILLES potential can be tested by its application to a number of specific molecules, for which the force field may be checked by means of a sufficient number of known observable properties. BILLES [1] has reported a successful application to ethylene. Our preliminary test for the totally symmetric species for benzene was also successful. On the other hand, the calculated force constants using the BILLES potential for boron trifluoride, boron trichloride and sulphur hexafluoride displayed results far apart from the conventionally accepted results.

SUMMARY

A discussion is given of the method of calculating force constants of molecular vibrations, as published by BILLES. The method is found to be approximate, in contrast to BILLES' statement; the nature of the inherent approximation is discussed.

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ANALYSIS OF STEROIDS, VI*

DETERMINATION OF PHENOLIC HYDROXYL CONTAMINATION OF OESTRONE ESTER DERIVATIVES

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Several derivatives of oestrone and oestradiol—esterified on the phenolic hydroxyl — are produced for the purpose of achieving prolonged oestrogenic effect. Most probable contaminants of these compounds are compounds containing free, not esterified hydroxyl groups. A volumetric method has been developed for the determination of these contaminants.

Recently we have published the solution of a similar problem: free phenolic hydroxyl contamination of 3-ether derivatives of oestrone was determined by titration with 0.1 *N* tetrabutyl ammonium hydroxide in an 1 : 1 mixture of tertiary butanol and toluene, using azo-violet as indicator [1].

The above method was tried also in the determination of free phenolic hydroxyl contamination in oestrone ester derivatives. It was found however, that the end point of the titration strongly shifted, the bluish colour of the overtitrated solution changes rapidly into green, therefore the results were difficult to evaluate, they were higher than the true value. This fact can easily be explained as follows: tetrabutyl ammonium hydroxide, being in excess after the end-point, decomposes the phenol-ester type compound present:

$$[(C_4H_9)_4N]\,OH + ArOAc = [(C_4H_9)_4N]OAc + ArOH$$

thus titrant is consumed also by the oestrone derivative itself. This reaction is so fast at room temperature that one cannot differentiate between the instantaneous neutralization of the phenolic hydroxyl, and the subsequent side-reaction. (GLENN and PEAKE [2] report on a similar reaction: ethylene diamine effects the aminolysis of phenolic esters. Acid amides and phenolic type products are formed in the reaction which is fast at room temperature.)

The above mentioned difficulties could be overcome by carrying out the titration at 0°C. In these circumstances the rate of the above side reaction is so low that the interferences are eliminated, and the determinations can be carried out at an accuracy attained in the determination of oestrone ether derivatives.

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* Part V. Acta Chim. Hung. **48,** 249 (1966).

Thus the method of the determinations was the one described previously, only the titration was carried out with ice-cooling.

Table I presents the results obtained in some model experiments.

Table I

Weighed sample			Found
Oestrone-3-acetate mg	Oestrone		Oestrone
	mg	%	%
353.0	5.3	1.5	1.6
350.1	11.7	3.2	3.1
347.1	12.5	3.5	3.8
347.5	22.0	6.0	6.0
Oestradiol-3-benzoate mg	Oestradiol		Oestradiol %
	mg	%	
403.6	9.2	2.2	2.1
332.8	9.8	2.9	3.1
Oestradiol-3,17-dipropionate mg	Oestradiol-17-propionate		Oestradiol-17-propionate %
	mg	%	
366.8	4.4	1.2	1.4
349.6	11.5	3.2	3.2
348.2	24.1	6.5	6.5

It can be seen that contaminants present in amounts higher than 1% can be determined with satisfactory accuracy.

We thank also here Miss M. KAPÁS for her useful work during the experiments.

SUMMARY

The method used previously for the determination of contaminants of oestrone ether derivatives was used for the determination of free phenolic hydroxyl contamination in oestrone ester derivatives. The titrations were carried out with tetrabutyl ammonium hydroxide, in a mixture of tertiary butanol and toluene, in the presence of azo-violet as indicator, under ice-cooling, in order to suppress the side reaction between tetrabutyl ammonium hydroxide and the oestrone ester derivative.

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INVESTIGATION OF THE THERMAL DECOMPOSITION OF ZIRAM AND ZINEB

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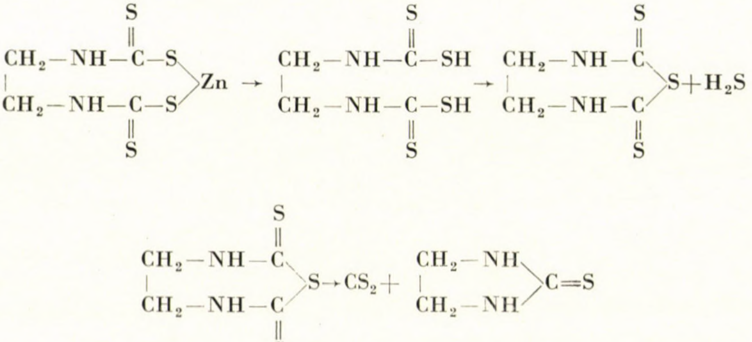
Among the fungicides of the dithiocarbamate type, used in chemical plant protection, the compounds containing zinc, Ziram (Zinc dimethyldithiocarbamate) and Zineb (zinc ethylene-bis-dithiocarbamate), are the most widely used [1, 2]. With these compounds, and in general with all the fungicides of dithiocarbamate type, stability is of very great importance from the point of view of their manufacture, storage, and application. Most of the plant protecting preparations, and particularly ethylene-*bis*-dithiocarbamates, decompose during storage upon action of light and moisture, and they lose their fungicide effect.

The decomposition of Ziram and Zineb was studied by several authors. GRANDI, CORTE and CIFFERI [3] investigated the decomposition of Ziram and Zineb at different temperatures in dependence on time, measuring their fungicid action. PETROSINI, TAFURI and BUSINELLI [4, 5] exposed Ziram and Zineb samples to the action of moisture and heat, and determined in function of the time the active substance in the samples. It was established by these authors that the decomposition of Zineb proceeds at a relatively high rate, and is promoted by insoluble copper salts, while Ziram proved to be more stable under similar conditions. They assumed that decomposition in the presence of moisture proceeds according to the following scheme:



Among the decomposition products, carbon disulphide, ethylenethiourea and zinc sulphide were identified. FISCHBEIN and FAWKES [6] investigated by paper chromatography the decomposition products of Zineb and Maneb (manganese ethylene-*bis*-dithiocarbamate). They established, besides that of ethylenethiourea, the presence of ethylenethiuram monosulphide, sulphur and an unidentified component in the decomposition products.

Though several patented processes are known for the stabilization of Zineb [7—10], stability is still an actual problem. Recent research work aims to attain a suitable control of the decomposition of Zineb by various additives [11, 12].

In our studies the thermal stability of Ziram and Zineb, the mechanism of their thermal decomposition was investigated by derivatography. This paper reports on the results of this analysis.

Experimental part

Preparation of the investigated compounds

1. *Ziram (zinc dimethyldithiocarbamate)*

The compound was prepared according to ISSOIRE and MUSSO [13] as follows: At room temperature, 0.2 mole of dimethylamine was reacted in form of a 20 per cent solution with 0.2 moles of carbon disulphide in the presence of 0.2 moles of sodium hydroxide. After the dissolution of carbon disulphide, the water-insoluble Ziram was precipitated with a 0.1 molar aqueous zinc sulphate solution. The precipitate was filtered, washed with water, and dried at 40°C under an infrared lamp. The yield was almost 100 per cent, and the zinc dimethyldithiocarbamate content of the product, determined by the method of CLARKE and coworkers [14], was found to be 99.7 per cent. The melting point of the compound, measured with a microscope with heatable stage, was 250°C, in accordance with data published in the literature [15].

2. *Zineb (zinc ethylene-bis-dithiocarbamate)*

The compound was prepared on the basis of a patent specification [16]: to a 20 per cent aqueous solution of 0.1 mole ethylenediamine 0.2 moles of carbon disulphide, and subsequently 0.2 moles of sodium hydroxide were added, and the mixture was stirred at room temperature until the complete dissolution of carbon disulphide. To eliminate trithiocarbonates, formed as by-products, the solution was neutralized with a 30 per cent acetic acid, using phenolphthalein as indicator, and Zineb was precipitated with 0.1 mole zinc sulphate. After two hours of stirring, the product was filtered, washed with water, and dried at 40°C under an infrared lamp. The zinc ethylene-*bis*-dithiocarbamate content was determined after decomposition with a mixture of pyridine and formic acid by the method of ROTH [17]. The quantity of the active substance present in various preparations varied within the range from 82 to 89 per cent. The product contained zinc sulphide as an impurity.

3. *Ethylenethiourea*

The compound was prepared by a process reported in the literature, involving the reaction of ethylenediamine in 50 per cent aqueous alcohol with carbon disulphide, and, after the addition of hydrochloric acid, boiling. After cooling with ice water, the product was filtered. The product precipitated in form of white needles, having a melting point of 202°C [18].

4. *Zinc trithiocarbonate*

0.1 mole of sodium sulphide was dissolved in 150 ml of water, and stirred at room temperature with 0.1 mole of carbon disulphide until the complete dissolution of the latter. Zinc trithiocarbonate was precipitated with zinc sulphate solution, the precipitate was filtered, washed with water, and dried at 40°C under an infrared lamp.

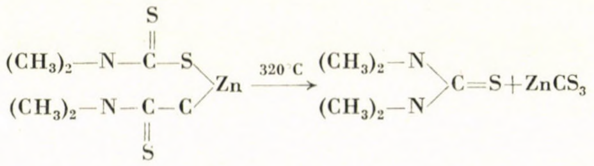
Derivatographic analysis

The derivatograms were recorded with a derivatograph of the system Paulik—Paulik—Erdey, manufactured by *MOM* [19], under nitrogen atmosphere. Reaction kinetic calculations were based on data of the TG and DTG curves [20].

Results and discussion

The thermal decomposition of Ziram

The derivatogram of zinc dimethyldithiocarbamate, recorded in nitrogen atmosphere, is shown in Fig. 1. The compound melts before decomposition, as indicated by the endothermic peak at 256°C on the DTA curve. In the literature, a melting point of 250°C is reported [15]. Thermal decomposition begins at 300°C, and is practically terminated at about 360°C. With the aid of the DTG curve, the TG curve can be divided into two sections, a loss in weight of 43.0 per cent assignable to the first DTG peak at 320°C, and a loss of weight of 25.2 per cent to the second DTG peak at 325°C. As a result of stoichiometric calculations, the decomposition can be represented by the following equation:



$$\left.\begin{array}{l}(CH_3)_2-N-\overset{\overset{\displaystyle S}{\|}}{C}-S\\(CH_3)_2-N-\underset{\underset{\displaystyle S}{\|}}{C}-C\end{array}\right\rangle Zn \xrightarrow{320\,^{\circ}C} \left.\begin{array}{l}(CH_3)_2-N\\(CH_3)_2-N\end{array}\right\rangle C{=}S+ZnCS_3$$

The theoretical weight loss corresponding to the splitting off of tetramethylthiourea according to the above equation is 43.4 per cent, which is in very good agreement with the measured value of 43.0 per cent. The formation of tetramethylthiourea is substantiated also by analogies known from literature: the thermal decomposition of tetramethylthiuram disulphide (TMTD, or the fungicide known under the name Thiuram), the oxidation product of sodium dimethyl-dithiocarbamate, was studied by Kuwaoka [21] and by Sahasrabudhey and Radhakrishnan [22], and it was shown that the thermal decomposition of this compound yields tetramethylthiourea, carbon disulphide and sulphur. Zinc trithiocarbonate, formed in the first decomposition step, is immediately decomposed with the corresponding DTG peak temperature of 325°C according to the following equation:

$$ZnCS_3 \xrightarrow{350^\circ C} ZnS + CS_2$$

The theoretical loss in weight assignable to this decomposition is 25.0 per cent, as compared to the measured loss in weight of 25.2 per cent.

Reaction kinetic calculations could be evaluated only for the first decomposition process, because the decomposition of zinc trithiocarbonate is not separated distinctly on the TG curve from the splitting off of tetramethylthiourea. The first decomposition process is a reaction of zero order, having an activation energy of —94.4 kcal/mole. It should be mentioned that among the investigated compounds of dithiocarbamate type, Ziram proved to possess the highest thermal stability.

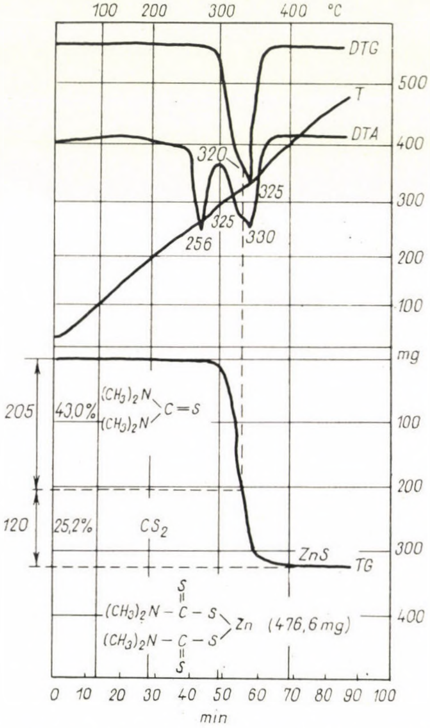
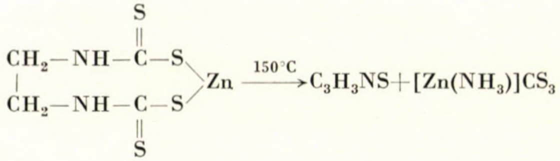


Fig. 1. The derivatogram of Ziram (zinc dimethyldithiocarbamate) in nitrogen atmosphere

The thermal decomposition of Zineb

The derivatogram of zinc ethylene-*bis*-dithiocarbamate (Fig. 2) shows that the decomposition begins already at about 100°C, at a substantially lower temperature than that of Ziram, and proceeds in three steps. From stoichiometric calculations on the basis of percentage losses, obtained from the curve, which can be divided according to the DTG peaks at 150, 225 and 300°C into three sections, the following decomposition mechanism was assumed:

1.



$$\left.\begin{array}{l}CH_2-NH-\overset{\overset{\displaystyle S}{\|}}{C}-S\\ |\\ CH_2-NH-\underset{\underset{\displaystyle S}{\|}}{C}-S\end{array}\right\rangle Zn \xrightarrow{150^{\circ}C} C_3H_3NS+[Zn(NH_3)]CS_3$$

2. $$[Zn(NH_3)]CS_3 \xrightarrow{225^{\circ}C} ZnCS_3+NH_3$$

3. $$ZnCS_3 \xrightarrow{300^{\circ}C} ZnS+CS_2$$

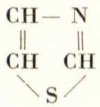
Calculated and measured weight losses for these three partial decomposition processes are as follows:

Loss in weight, %

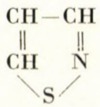
	Calculated	Measured
1.	30.9	30.9
2.	6.2	6.3
3.	27.7	27.5

Kinetical calculation could be carried out for the first and the third decomposition process. Pertinent curves are plotted in Fig. 3. According to the data of this diagram, the first decomposition process is of the order −0.2, that is to say, practically zero, with an activation energy of −24.5 kcal/mole, while the order of reaction of the third decomposition process, *i.e.* of the decomposition of zinc trithiocarbonate is +1, and its activation energy −30.5 kcal/mole.

The compound formed in the first decomposition step of the composition C_3H_3NS, can be thiazole or isothiazole:



or



(Thiazole) (Isothiazole)

Several experiments were carried out to verify the assumed mechanism of the decomposition. To establish whether thiazole or isothiazole is formed in the first step of the decomposition, about 30 g of Zineb was weighed into a spherical

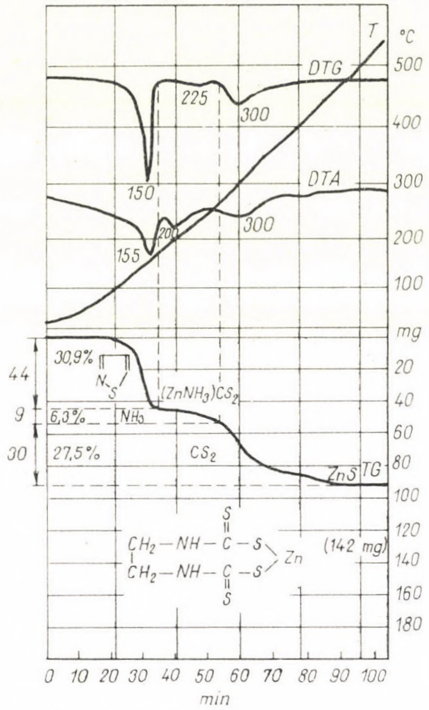


Fig. 2. **The derivatogram of Zineb (zinc ethylene-*bis*-dithiocarbamate) in nitrogen atmosphere**

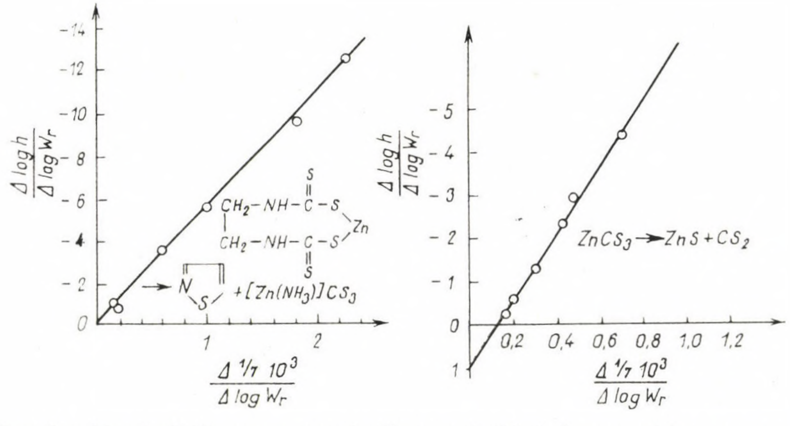
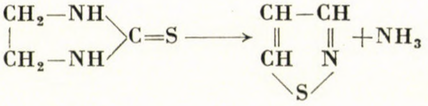


Fig. 3. **Reaction kinetical diagrams on the first and third decomposition steps of Zineb**

flask, equipped with reflux-condenser and thermometer, and kept for 4 hours at 300°C. The liquid formed in the decomposition was separated from the yellow solid residue, which was shown by separate tests to be zinc sulphide. The liquid formed two inmiscible phases. After separation and careful rectification, one of the phases was identified as carbon disulphide. The other part, distilling in the range from 106 to 110°C, was a pale yellow liquid of very obnoxious odour, readily soluble in water. The sulphur content of this liquid was determined and found to correspond to the composition C_3H_3NS (calculated sulphur content 37.7 per cent, found 38.2 per cent).

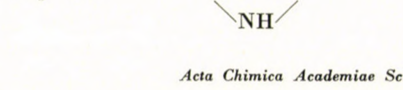
According to data in the literature, at a pressure of 770 torr the boiling point of isothiazole is 113°C, that of thiazole 117°C; both compounds are bases readily soluble in water, the melting point of the hydrochloride of thiazole being 138°C [23]. Data on the melting point of the hydrochloride of isothiazole are not available in the literature. As the boiling point of our decomposition product comes nearer to that of isothiazole, and its readily crystallizing hydrochloride does not melt up to 200°C, it can be assumed indirectly that isothiazole is formed in the decomposition.

On the basis of this experiment it was assumed that — in accordance with the data of literature — in the decomposition of Zineb ethylenethiourea and zinc trithiocarbonate are formed as intermediate products, and ethylenethiourea is decomposed into isothiazole and ammonia:



Ammonia, formed by the decomposition of ethylenethiourea, gives with zinc trithiocarbonate a monoammine complex. (The diammine complex can be obtained preparatively, and is a well known compound [24]).

To verify our assumption, ethylenethiourea was prepared and investigated by derivatography (Fig. 4). The endothermic peak appearing at 200°C on the DTA curve, indicates the melting point. The decomposition of the compound, as shown by the peak temperatures at 290 and 305°C on the DTG curve, proceeds in two steps. However, the decomposition products indicated by the percentage weight losses were not isothiazole and ammonia, but — as proved also preparatively — hydrogen sulphide and imidazole (glyoxaline), according to the following reaction scheme:



On decomposing a greater quantity of ethylenethiourea at 300 to 320°C in a spherical flask, besides hydrogen sulphide, to be detected qualitatively, a decomposition product melting at 89 to 90°C is obtained, the nitrogen content of which corresponds to the composition $C_3H_4N_2$ (nitrogen content: calculated 41.1 per cent, found 42.3 per cent). This empirical formula corresponds to the composition of both imidazole (glyoxaline) and pyrazole. However, the melting point of imidazole, reported in literature, is 88 to 89°C, while that of pyrazole 69 to 70°C [25], so that the formation of imidazole can be considered as proved on the basis of the melting point of the decomposition product.

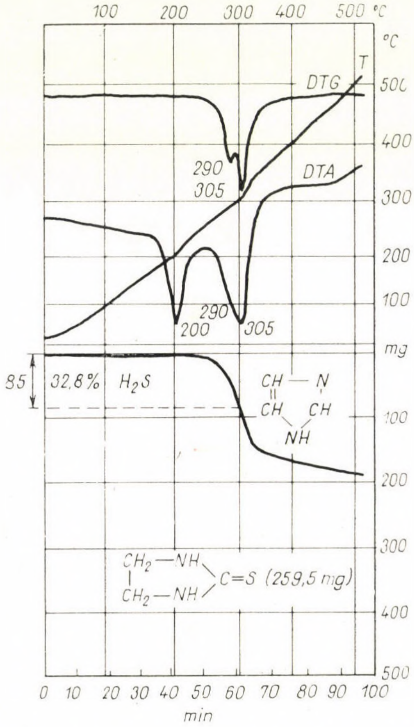


Fig. 4. The derivatogram of ethylenethiourea in nitrogen atmosphere

On the evidence of these investigations, our assumptions pertinent to the decomposition of ethylenethiourea had be modified in the sense that ethylenethiourea is decomposed to isothiazole and ammonia only in the case when a substance is present in the system, which can bind ammonia in some relatively stable form, thus, in our case, in form of a complex compound. This precondition is realized in the case of Zineb, or more accurately, in the presence of zinc trithiocarbonate, formed by the decomposition of Zineb. As shown by the derivatogram in Fig. 2, the intermediate complex is stable up to about 220°C, to decompose at the DTG peak temperature of 225°C. In the absence of a substance capable to bind ammonia, ethylenethiourea is decomposed to hydrogen sulphide and imidazole.

Further experiments were carried out to prove this modified assumption. Zinc trithiocarbonate was prepared and studied by derivatography. According to our investigations, zinc trithiocarbonate is decomposed at a DTG peak temperature of 125°C, the order of reaction, similar to that of carbonates, being +1, as may be seen from data in Fig. 3. The derivatogram of a 1 : 1 molar mixture of ethylenethiourea and zinc trithiocarbonate was recorded. Although the TG curve of this derivatogram does not permit to establish an unequivocal relationship, a certain information can be obtained on the solid phase reaction between ethylenethiourea and zinc trithiocarbonate. The thermal decomposition proceeds at a DTG peak temperature of 110°C, and also the DTA curve presents at 120°C a great endothermic decomposition peak, however, the melting point of ethylenethiourea at 200°C is absent on the DTA curve, so that the reaction between ethylenethiourea and zinc trithiocarbonate can be considered as proved.

Also in this case, the decomposition products of an 1 : 1 molar mixture of ethylenethiourea and zinc trithiocarbonate, kept at 300°C, were investigated. Though a slight evolution of hydrogen sulphide could be detected qualitatively, the analysis of the liquid decomposition products, similarly as in the case of Zineb, indicated the formation of isothiazole and carbon disulphide, while no imidazole could be detected in the decomposition products.

Analytical possibilites

The elucidation of the reaction mechanism of the decomposition, described in the preceding part, offered a possibility for analytical determinations on the basis of the derivatograms, particularly in the case of ethylene-*bis*-dithiocarbamates. The total loss in weight presented on the derivatograms of various Zineb preparations gives information on the purity of the compound, provided that the impurities which are present do not decompose in the investigated temperature range, that is to say up to about 500 to 600°C, a precondition met *e.g.* by zinc oxide or zinc sulphide.

Several analyses were carried out to determine the purity of Zineb preparations obtained under various conditions. Results of these determinations, as compared to analytical data obtained by the acid decomposition method in current use, are presented in Table 1.

The accuracy of the two methods is about the same, and they require about the same time. However, derivatography proved to be more accurate, when the preparation contained also impurities which are decomposed in the

A further example for our derivatographic method of analysis involves the investigation of a Maneb preparation, where the sodium ethylene-*bis*-dithiocarbamate solution has been neutralized before the precipitation of Maneb with manganese chloride, and therefore our product contained also manganese trithiocarbonate. The derivatogram is shown in Fig. 5. The manganese ethylene-*bis*-dithiocarbamate content can be calculated from the second and third sections of loss in weight, however, the percentage value of the first section of loss weight is greater than would correspond to the splitting off of isothiazole. The difference stems from the splitting off of the carbon disulphide of manganese trithiocarbonate, and thus, the percentage quantity of the latter can be calculated from this difference. From the total loss in weight and from the weight of the sample, the manganese sulphide content of the sample can be calculated. On the basis of the data of the presented derivatogram, the composition of the analysed sample was the following:

Manganese ethylene-*bis*-dithiocarbamate	75.1 per cent
Manganese trithiocarbonate	16.8 per cent
Manganese sulphide	7.9 per cent

The method developed by us is suitable also for plant control, and may be more advantageous than the acid decomposition method.

For help in experimental work, we wish to thank Miss E. DECHATEL, laboratory technician and Miss ZS. LIGETFALUSI, laboratory assistant.

SUMMARY

The thermal decomposition of Ziram and Zineb was investigated, and the reaction mechanism of the decomposition cleared. The decomposition of Ziram proceeds at the DTG peak temperatures 320 and 325°C, yielding as decomposition products tetramethylthiourea and carbon disulphide. In the decomposition of Zineb ethylenethiourea is formed as an intermediate product subsequently decomposed to isothiazole and ammonia; ammonia gives, with zinc trithiocarbonate formed in the decomposition, a relatively stable complex, which is decomposed in the second step. In the third step of the decomposition, the zinc trithiocarbonate is decomposed into carbon disulphide and zinc sulphide. Investigations showed that ethylenethiourea is decomposed into isothiazole and ammonia only when the system contains also a substance which can bind ammonia, or else the decomposition products are hydrogen sulphide and imidazole. Derivatography can be used also as an analytical method, for the determination of the active substance.

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ACTA CHIMICA

ТОМ LI

РЕЗЮМЕ

ОСАДОЧНОЕ РАЗДЕЛЕНИЕ СЛЕДОВ ЭЛЕМЕНТОВ, II. МЕХАНИЗМ СОРБЦИИ УРАНА (VI) ИЗ КАРБОНАТНОЙ СРЕДЫ. ДЕСОРБЦИОННОЕ ВЛИЯНИЕ ГИДРООКИСИ ТОРИЯ

Э. УПОР

Для выяснения причин потерь, выступающих при разделении урана (VI) из карбонатной среды, растворы, содержащие ионы $(UO_2(CO_3)_3)^{4-}$, обрабатывались различными адсорбентами. Установлено, что независимо от химической природы адсорбентов потеря урана почти полностью происходит благодаря распаду комплекса и связыванию ионов UO_2^{2+}. Исследовалась способность связывания урана на окисях, гидроокисях и фосфатах металлов. Найдено, что в экспериментальных условиях на гидроокисях и фосфатах, примененных в качестве неорганических ионообменников, эта величина $>$ 1 мэкв/г.

Обстоятельно исследовалось десорбционное воздействие гидроокиси тория. Установлено, что это воздействие осуществляется от pH 7,7 до pH 13, и в его присутствии не выступает второй максимум, вызываемый гидроксильными ионами. Это десорбирующее влияние объясняется главным образом тем, что вследствие большой способности $Th(OH)_4$ связывать карбонат, а также вследствие низкой основности этого соединения связывание гидроксильных ионов является незначительным. Снималась зависимость адсорбции карбоната и гидроксильного иона на $Fe(OH)_3$ и $Th(OH)_4$ от величины pH. Результаты в полной мере объясняют зависимость адсорбции урана от pH. Увеличение адсорбции урана, происходящее совместно со старением осадка, объясняется опять-таки отсутствием связывания иона карбоната. Исследовалось возможное десорбирующее действие других катионов (Zr^{4+}, La^{3+}, Ce^{3+}, Y^{3+}, Zn^{2+}, Be^{2+}). Найдено, однако, что десорбирующее действие тория на $Fe(OH)_3$ является специфическим. Цирконий и лантан, при анализе породы, в небольшой степени снижают адсорбционные потери. Объясняется это тем, что в присутствии этих соединений, если даже и не имеет место возрастание карбонатной адсорбции, связывание гидроксильных ионов является незначительным.

НЕСКОЛЬКО ВОПРОСОВ ОСАДОЧНОГО РАЗДЕЛЕНИЯ СЛЕДОВ ЭЛЕМЕНТОВ III. ОТДЕЛЕНИЕ МАЛЫХ КОЛИЧЕСТВ УРАНА (VI) ОТ ГИДРООКИСЕЙ МЕТАЛЛОВ С ПОМОЩЬЮ ГИДРООКИСЕЙ ЩЕЛОЧНЫХ МЕТАЛЛОВ. ИССЛЕДОВАНИЕ СОСТАВА ПЕРЕОСАЖДЕННОГО УРАНА

Э. УПОР

Исходя из ранних исследований (проведенных в связи с карбонатным разделением урана (VI)) более подробно изучалось поведение урана (VI) в среде гидроокиси щелочного металла. Установлено, что находящийся в малых количествах уран (VI) количественно выпадает на гидроокиси железа (III) до pH = 12, затем, с увеличением pH уран постепенно переходит в раствор. Растворение при pH = 13—14 является количественным, если концентрация урана равна 5.10^{-4} M. С увеличением концентрации электролита, а также со временем растворимость снижается. Исследовался состав осадка, разделенного с помощью NaOH при высших концентрациях урана (0,005—0,02 М/л); установлено, что в области pH = 11,9—13 соотношение Na: U в осадке равно 1,00 ± 0,04. Это соответствует составу $Na_2U_2O_7$, следовательно, предположение нескольких авторов о существовании в данной области pH Na_2UO_4 не является обоснованным. В растворе NaOH большей концентрации, а также при длительной стоянке, соотношение Na: U повышается до 1,25. Наиболее вероятным объяснением этого является совместноосаждение NaOH.

Значительная адсорбция (OH^-) NAOH подтверждается также и тем фактом, что переход урана в раствор является коллоидным явлением. Последнее было подтверждено электронно-микроскопическими снимками.

Растворение урана (VI) в щелочной среде может быть использовано для целей препаративной и аналитической химии. До сих пор, в первую очередь, внедрено разделение урана от тория, не только для определения содержания тория в урановой руде, но и для получения UX_1, а также для радиохимической очистки урана.

СПЕКТРОСКОПИЧЕСКОЕ ОПРЕДЕЛЕНИЕ ВАНАДИЯ И НИКЕЛЯ В НЕФТЯНОЙ ЗОЛЕ

А. ПЕТЁ

Разработан метод спектрографического определения V и Ni для зол венгерских нефтей. Нефти очищались и обезвоживались центрифугированием, затем применялась медленная сернокислая разгонка. В случае последней к 100 г. масла добавлялось 10—20 капель концентрированной серной кислоты, что предотвращало потерю V и Ni. Зола смешивалась в соотношении 1 : 3 с порошком SiO_2, содержащим 1% Co, затем смесь примешивалась к спектрально чистому порошкообразному графиту, в соотношении 1 : 2. Эта спектрографическая смесь возбуждалась в отверстии графитного электрода. Даются параметры возбуждения, аналитические и относительные линии, с относящимися к ним пределами измерений и воспроизводимостью. Чувствительность анализа равна 0,005%, верхний предел составляет 30% по отношению к нефтяной золе.

АНАЛИЗ ЗАГРЯЗНЕНИЙ В НИКЕЛЕ ВЫСОКОЙ ЧИСТОТЫ

М. ЧАЙКА, М. ЁРДЁГ и Э. САБО

Разработан метод определения загрязнений, важных с точки зрения техники связи, в катодовом никеле с помощью активационного анализа. Отдельные элементы разделялись с помощью ионного обмена, непосредственно после облучения. Метод дает возможность систематического анализа следующих элементов: мышьяка, меди, сурьмы, цинка и висмута.

ТЕОРИЯ НЕКОТОРЫХ ФОТОХИМИЧЕСКИХ ПРОЦЕССОВ ПРИ НИЗКИХ ТЕМПЕРАТУРАХ

ДЖ. Х. ПЭРНЕЛЛ

Рассматриваются последние работы по аналитическому изучению продуктов фотолиза HI и CH_3I в реакционноспособных углеводородных матрицах при 77° K. Делается заключение о том, что результаты находятся в лучшем соответствии с предположением о фотолизе рыхлых комплексов матрица-молекулы вещества, подвергаемого фотолизу, чем о фотолизе непосредственно самих молекул веществ. Приводятся возможные структуры комплексов типа $[R — I]_2$ и $[RI — M]$, с помощью которых можно объяснить образование найденных продуктов. На основе настоящего представления удалось качественно объяснить механизм образования продуктов низкотемпературного фотолиза CH_3NO_2 и CH_3ONO.

ЗАВИСИМОСТЬ МЕЖДУ ПРОЧНОСТЬЮ СВЯЗИ И КОЛЕБАТЕЛЬНЫМИ СИЛОВЫМИ ПОСТОЯННЫМИ

Ш. СЁКЕ

Валентные силовые постоянные двухатомных молекул зависят от электроотрицательности, длины и энергии связи. В целом ряде молекул, имеющих в большинстве случаев ковалентный характер, фактор пропорциональности является приблизительно постоянным. Силовые постоянные двухатомных гомо- и гетеро-ядерных молекул могут быть рассчитаны друг из друга. Если ионным характером пренебречь нельзя, то нужно применять корреляцию на основе ионковалентной резонансии. Приведена зависимость между прочностью связи и силовыми постоянными.

О РАСЧЕТЕ ЭНЕРГИИ РЕШЕТКИ КАРБИДОВ ЩЕЛОЧНО-ЗЕМЕЛЬНЫХ МЕТАЛЛОВ (CaC_2, SrC_2, BaC_2) И ЭНЕРГИИ ДИССОЦИАЦИИ АЦЕТИЛИДНОГО ИОНА

Г. ВИНЕК, А. НЕКЕЛЬ и Х. НОВОТНИ

Были рассчитаны энергии решетки CaC_2, SrC_2 и BaC_2 с учетом несферического распределения заряда в ацетилидном ионе. Из этих данных были оценены теплота образования иона $C_2^{=}$ по

$2C$ (графит) $+ 2\bar{e} = C_2^{=}$ (г), $X = 220$ ккал/моль и энергия диссоциации (D) по $C_2^{=}$ (г) $= 2C^{-}$ (г), $D = 66$ ккал/моль.

ПРИБЛИЗИТЕЛЬНОЕ ВЫЧИСЛЕНИЕ ЭНТРОПИЙ И ЭНТАЛЬНЫХ СВОБОДНЫХ РАДИКАЛОВ. I. СТАТИСТИЧЕСКИЙ РАСЧЕТ ЭНТРОПИЙ

Ш. ФЕРГЕТЕГ и Т. БЕРЦЕШ

Вычислены энтропии некоторых простых, принадлежащих к разным типам, свободных радикалов статистическим термодинамическим методом. В течении расчетов мы пользовались молекулярными данными, с подходящими предположениями относительно структурных разностей между свободными радикалами и родильными („parent'') молекулами. Обсуждалась точность вычисленных значений энтропии. Мы коснулись применимости одного приблизительного метода для оценки энтропий свободных радикалов, основанного на энтропиях молекул.

ПОТЕНЦИАЛ БИЛЛЕША ДЛЯ МОЛЕКУЛЯРНЫХ КОЛЕБАНИЙ

С. Й. СИВИН, Л. А. КРИСТИАНСЕН и ДЖ. БРУНВОЛЛ

Обсуждается предложенный Биллешом метод расчета силовых постоянных молекулярных колебаний. Упомянутый метод — в отличие от мнения автора — носит лишь приближенный характер. Обсуждается степень приближенности, скрытая в самом методе.

АНАЛИТИКА СТЕРОИДОВ, VI

Ш. ГЁРЁГ

Для определения свободного фенольного гидроксила, находящегося в качестве загрязнений в производных сложных эфиров эстрона, применялся метод, описанный автором ранее для аналогичных исследований производных сложных эфиров эстрона. Титрование гидро-окисью тетрабутил-аммиака в смеси трет-бутанол-толуол, при использовании в качестве индикатора азо-фиолетового, проводилось при охлаждении льдом, для подавления мешающей реакции между гидроокисью тетрабутил-аммиака и производным эфира эстрона.

ИССЛЕДОВАНИЕ ТЕРМИЧЕСКОГО РАСПАДА ЦИРАМА И ЦИНЕБА

ДЬ. ПФЕЙФЕР и Т. ФЛОРА

Исследовался термический распад Цирама и Цинеба и был выяснен механизм реакции распада. Согласно дериватографическим исследованиям, распад Цирама (диметил-дитиокарбамат цинка) проходит при пиковой температуре ДГТ 320—350°, продуктами распада являются тетраметил-тиокарбамид и CS_2. В случае распада Цинеба (этилен-бис-дитиокарбамат цинка) образуется промежуточно этилен-тиокарбамид, распадавшийся в изо-тиазол и аммиак; аммиак дает сравнительно устойчивое комплексное соединение с тритиокарбонатом цинка. Этот комплекс распадается во второй ступени. В третьей ступени распада тритиокарбонат цинка распадается на CS_2 и сульфид цинка. Согласно исследованиям, этилен-тиокарбамид распадается только в том случае на изотиазол и аммиак, если в системе присутствует вещество, способное связывать последний. В противном случае продуктами распада являются сероводород и имидазол. Дериватография может быть использована и в качестве аналитического метода, для определения содержания эффективного вещества.

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Table 1

Percentage zinc ethylene-bis-dithiocarbamate

Derivatography	Acid decomposition
74.5	74.1
79.2	78.5
85.0	82.5
86.5	86.3

temperature range, investigated and thus, affect the acid decomposition method. Primarily, trithiocarbonates have to be considered as impurities of this kind. Besides for Zineb, derivatographic analysis is suitable also for the analysis of Maneb, a compound of similar type (manganese ethylene-*bis*-dithiocarbamate). The decomposition mechanism of this compound was investigated by the method described for Zineb, and was found to be analogous to that of Zineb.

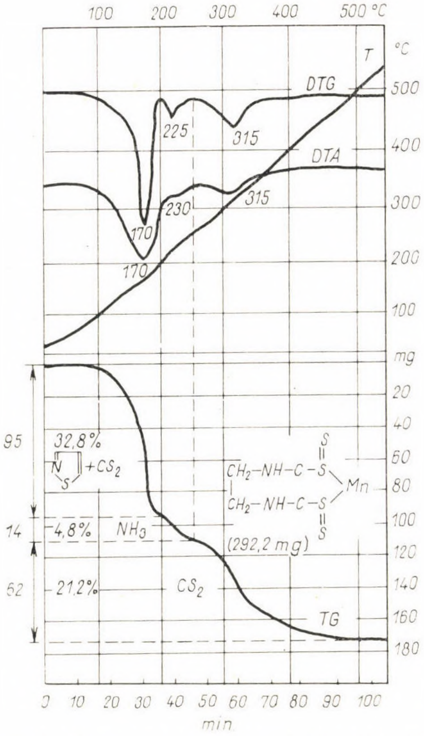

Fig. 5. The derivatogram of Maneb (manganese ethylene-*bis*-dithiocarbamate) in nitrogen atmosphere

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USE OF DIELECTROMETRY IN UP-TO-DATE INDUSTRIAL CHEMICAL ANALYSES

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Received May 6, 1966

Analytical methods recently evolved make possible the testing of chemical products in the course of their manufacture. As far as rapidity, simplicity, and reliability are considered, dielectrometric test methods have assumed a rather important role in the control of chemical operations [1] and processes [2, 3, 4].

Analitical applications of the "Universal Dielectrometer"

In collaboration with GÉZA SZABÓ an instrument: *"Universal Dielectrometer"* [5, 6] has been constructed which proved useful in quality control, especially for frequent routine tests. *E.g.*, in the production of polyhalogenated derivatives of acetylene, a rapid method of on-line quality control is afforded by measuring the dielectric constants of the binary systems trichloroethylene—tetrachloroethane, tetrachloroethane—tetrachloroethylene, and pentachloroethane—trichloroethylene [7].

In the sulphochlorination of gas oil, the reaction product may be analyzed on the basis of the microamperes measured and plotted against the progress of saponification. This curve is shown in Fig. 1.

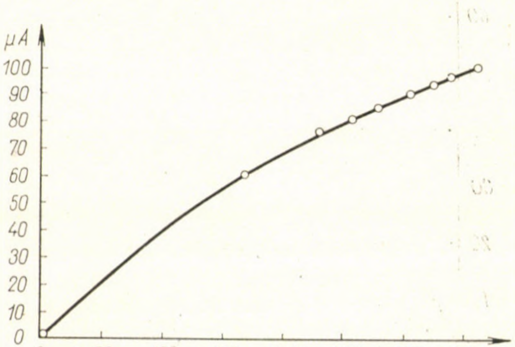

Fig. 1. Dielectric constant curve, microamperes *vs.* saponification number for sulphochlorinated gas oil

In some cases lengthy chemical analyses *via* functional groups [7], such as halogene, hydroxyl, epoxide, *etc.*, can thus be dispensed with. Dielectrometry is a rapid and reliable method for the evaluation of the effect of catalysts, accelerators, antioxidants, emulsifiers. In combination with the determination of another physical constant, dielectrometry can be used as a rapid on-line test method for ternary systems [2]. Dielectrometric titration especially of binary and of ternary systems difficult to titrate by classical methods is rather important. The effectiveness of molecular sieves in industry, especially in the drying of solvents, can be readily ascertained by dielectrometry; on the other hand, molecular sieves play an important role in the development of gas chromatography and differential dielectrometric titrations. Dielectrometry includes the measurement of loss factors, and this is an important feature in establishing purity-grades, molecular structures, and investigation of polymer substances.

Dielectrometric indication

In addition to testing good dielectrics, dielectrometry is sometimes also applicable for the indication of the end-point of reactions, utilizing the so-called non-polar solvent effect. *E.g.*, in the sulphation of fatty alcohols with chlorosulphonic acid, samples of the same volume are taken from the reac-

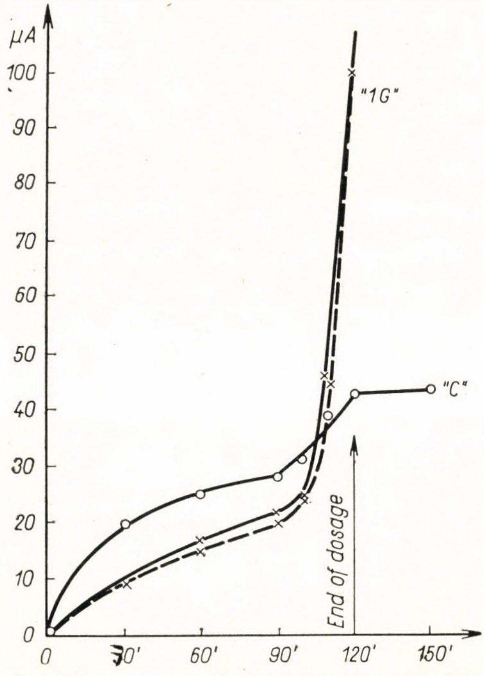

Fig. 2. Registering by dielectrometry of the sulphation of a fatty alcohol, PF—8. C = capacitance position, G = loss position

tion mixture and mixed with the same volume of a non-polar solvent, such as petroleum ether. The completion of a sulphation reaction of PF-8 alcohol is indicated in Fig. 2; in Fig. 3 the sulphation of lauryl alcohol is shown as registered by a transistorized instrument, and by the original laboratory instrument. It can be seen that the former gives the same reading but with a deflection in the opposite direction.

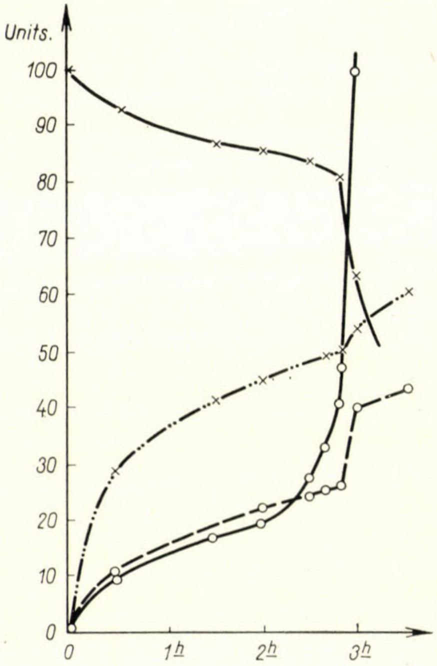

Fig. 3. Following by dielectrometry of the sulphation of lauryl alcohol: comparison of two instruments

- - - - -○ instrument with electron valves, in position *C;* ———○ instrument with electron valves, in position *G;* — · · × instrument, transistorized, in position *C;* ——— × instrument, transistorized, in position *G*

Elimination of the effects due to the temperature dependence of ε

The principal difficulty in the use of dielectrometry for chemical process control is the elimination of the effect which temperature exerts upon dielectric constants. This problem has been solved in several ways.

1. By means of calibration curves plotted for various temperatures (Fig. 4).

2. The measuring cell of the instrument is jacketed and kept at a suitable constant temperature which is in accord with, but not necessarily the same

as the temperature of, the reaction mixture. Samples for the dielectric measurement of this reaction mixture are transferred into the cell so that at their arrival there they have the temperature of the cell. Calibration curves are taken at cell temperatures. After dielectric measurement, the sample is allowed to return into the reactor. This method proved feasible and suitable in on-line analyses in the manufacture of dioctyl phtalate [2]. For this sampling technique the term harmonic sampling has been coined.

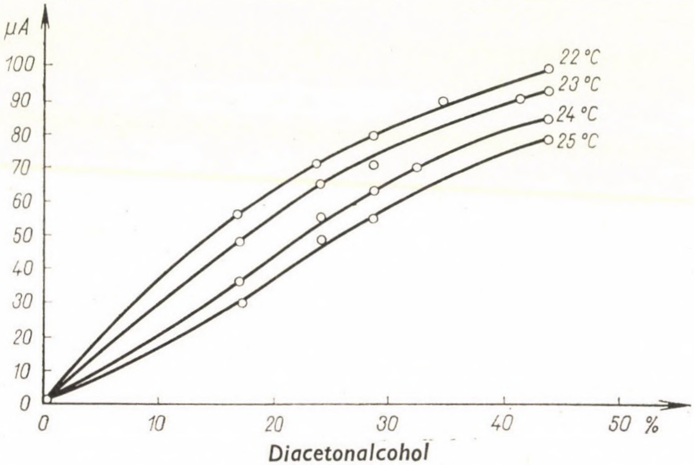

Fig. 4. Dielectric constant curve, microamperes *vs.* weight per cent, for acetone-diacetone alcohol mixtures

3. For use in the chemical industry perhaps an instrument with two oscillators (Fig. 5) is the best for the compensation of the temperature dependence of dielectric constants.

To each of the oscillators a measuring cell made of stainless steel and polyamide, and having exactly the same capacitance, is connected. The solvent of variable temperature flows through cell C_{XI} and then into the jacket of cell C_{XII}. The latter cell is filled with a substance the dielectric constant of which is very nearly the same as that of the solvent flowing through cell C_{XI}. Thus the solvent that has passed through cell C_{XI} keeps the temperature of the liquid in the compensation cell C_{XII} at temperatures corresponding to its own. Consequently, the two cells with nearly the same capacitance affect the amplitudes of the two oscillators equally, and the pointer of the meter is not deflected.

Plant dielectrometer and its application in industrial practice

From the laboratory model a new process instrument has been evolved which is suitable being mounted on, or connected to, manufacturing apparatus (Fig. 6).

1. The oscillator part is built into the measuring head; the indicator or meter, together with the power supply unit, forms a separate part.

2. The process instrument does not measure but capacitance and resistivity loss by the deflection method, because there is no calibrated rotating condenser in the instrument.

3. When capacitance is measured with the process instrument, maximum and minimum limits are to be fixed, respectively, by the tuning of built-in oscillatory circuits, thus the zero-point maximum deflection of the meter can be checked at any instant during measurement. This is the most important condition to be fulfilled in the case of a continuous control during manufacture.

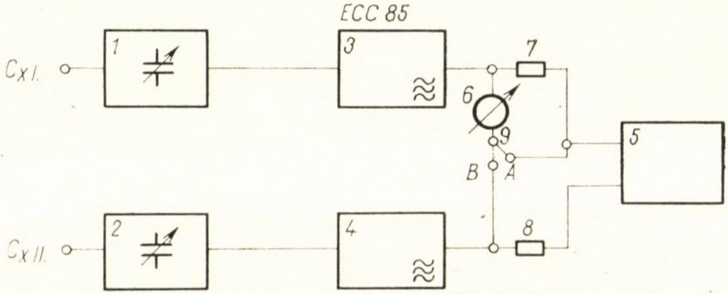

Fig. 5. Instrument with compensation of the temperature effect by two oscillators
1, 2 auxiliary oscillator circuits; 3, 4 electron valve oscillators; 5 stabilized anode; 6 meter; 7, 8 resistors; 9 switch

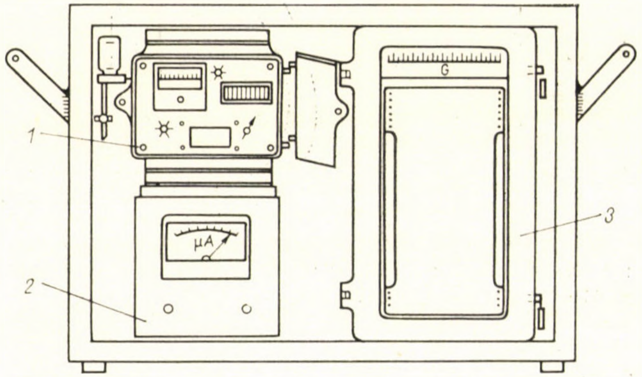

Fig. 6. Process dielectrometer. 1 measuring head; 2 meter; 3 recorder

For on-line quality control, cells and probes made of stainless steel and Teflon proved very useful; developing these we evolved a construction, shown in Figure 7, of a process dielectric cell with flexible connection. Having suitable flanges, these cells can be mounted directly on manufacturing apparatus.

For more than a year and a half this type of dielectrometric instrument has been used with good results for the control of an acetic anhydride plant. Fig. 8 presents some curves of dielectric constants for mixtures of acetic acid and acetic anhydride, microampere *vs.* composition being plotted in the zero to 2% or zero to 70% acetic acid concentration range. Since the dielectric constant of acetic acid is 6.17 and that of acetic anhydride 22.2 the zero point of the process instrument was fixed with mixtures of high acetic acid content, *i.e.* with those of low dielectric constant, and the maximum deflection was used for pure acetic anhydride.

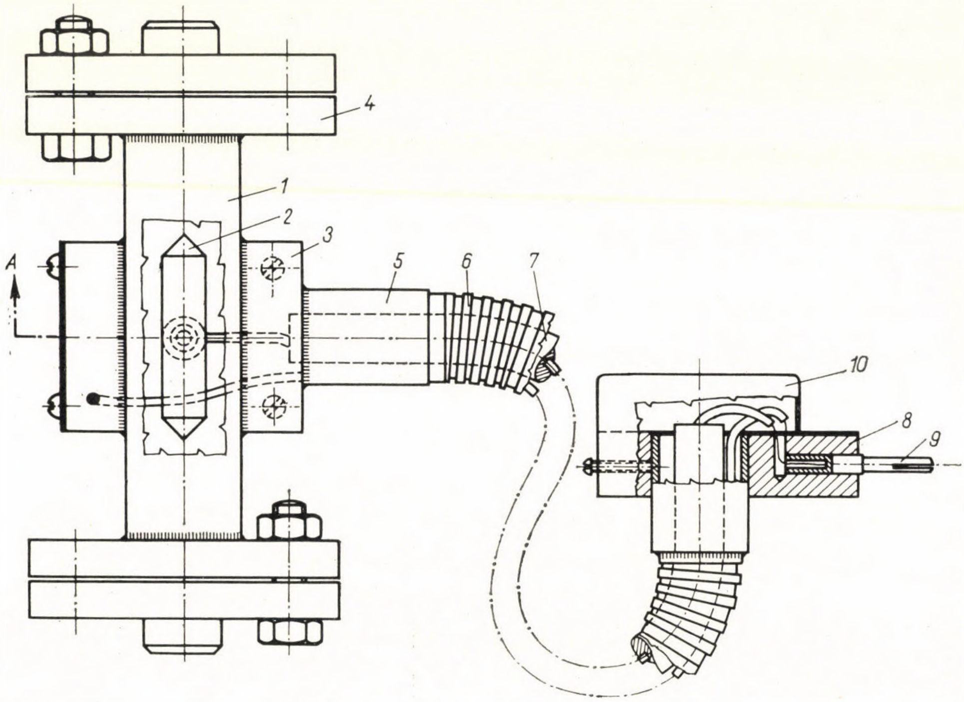

Fig. 7. Cell for the process instrument
1 outer armature; 2 inner armature; 3 support; 4 flanges; 5 rigid tube; 6 flexible lead; 7 insulation; 8 support (bakelite); 9 plug connector; 10 screening box

The following table shows a comparison of results.

In this anhydride plant the indicator part of the dielectrometer was mounted on the instrument panel of the central control room. This process dielectrometer was successfully applied also in the routine analysis of mixtures of acetone and diacetone alcohol, and acetone and water produced in the manufacture of diacetone alcohol, further in the analysis of toluene-benzyl chloride mixtures in the manufacture of the latter.

Acetic anhydride per cent found		
Classical method		Industrial dielectric instrument
plant control lab.	chemical lab.	
99.25	99.00	98.50
98.64	99.00	98.50
47.00	49.00	47.30
99.90	99.50	100.00
96.00	98.00	96.50
98.23	98.50	98.50
	79.00	79.50
known acetic anhydride content, %		
54.60		54.50
14.80		15.00
0.50		0.54

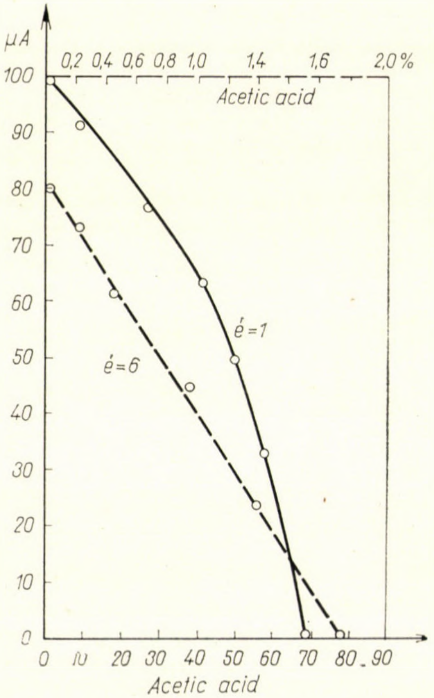

Fig. 8. Dielectric constant curve, microamperes *vs.* weight per cent, for acetic acid and acetic acid anhydride mixtures

- - - - - 0—2% acetic acid; ——— 0—70% acetic acid; é = sensitivity

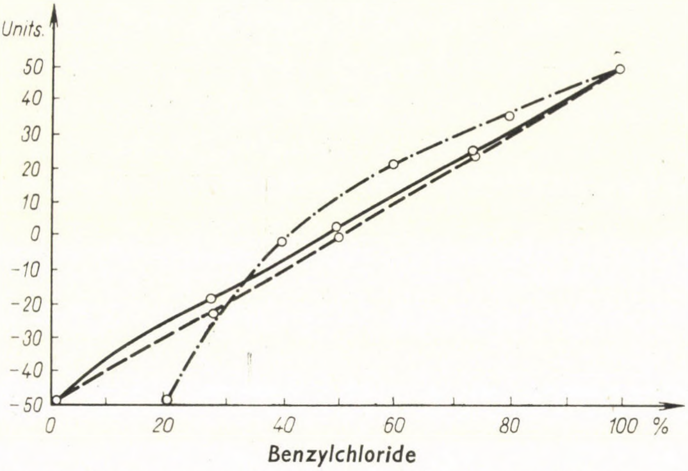

Fig. 9. **Dielectric constant curve, meter units *vs.* weight per cent, for toluene-benzyl chloride mixtures**

——— **Treated with HCl, measured with the *Universal Dielectrometer;*** - - - - - Not treated **with HCl,** measured with the *Universal Dielectrometer;* — · — Measured by means of the process instrument

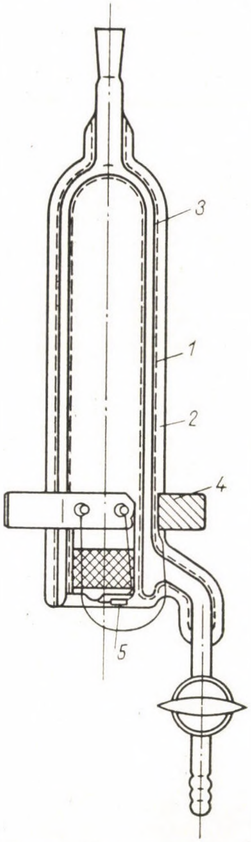

Fig. 10. Electrodeless capacitive cell

1 metal film; 2 protective laquer coating; 3 glass; 4 plastic support; 5 condenser in series

Fig. 9 shows the meter units *vs.* benzyl chloride concentration curves used in the analysis of reaction products from the chlorination process of toluene to benzyl chloride, plotted with a laboratory and a process instrument, respectively. This figure shows that dielectrometry can be carried out also in the presence of HCl.

Sometimes, *e.g.*, with chloride, it is better to use electrodeless cells to obviate difficulties due to corrosion. Such a cell is shown in Fig. 10, where the thin layer covering the glass is coated with a plastic film [8] to protect it against abrasion.

To summarize: together with the *Universal Dielectrometer* already on the market, the transistorized plant and laboratory instruments described can do important service in up-to-date industrial analyses. This transistorized instrument has been designed for plants where inflammable vapours may occur.

The author wishes to thank Mr. GÉZA SZABÓ, electronic engineer, Mrs. T. SEBESTYÉN and Mrs. F. VARGA for their valuable help in these researches.

SUMMARY

Dielectrometric measurements, carried out with the help of a "process dielectrometer" and a special cell connected to it by a flexible lead, are rapid, simple, and reliable, thus readily applicable to the control of chemical processes and operations by the characterization of mixtures such as acetic acid and acetic acid anhydride, or toluene and benzyl chloride, etc. To counteract disturbing effects due to the temperature of the dielectric constant, the best method found is a so-called harmonic-sampling procedure and temperature compensation by a double-oscillator dielectrometer. The best method for the control of sulphation and for the indication of its end-point is the application of the non-polar solvent effect combined with registering of the change in loss-resistance.

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DETERMINATION OF IRON BY CHELATING RADIOMETRIC TITRATION

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Radioactive indicators can be used in volumetric analysis to determine the point of equivalence. The significance of these "radiometric titrations" has markedly increased in the past years [1, 2, 3].

The separation of reaction products formed from the initial components during titration can be also done by ion exchangers. Ion exchange separation for the end point indication of chelating radiometric titrations was first suggested and used by Schumacher and Friedli [4], then by Stary, Ruzicka and Zeman [5]. Ion exchange separation was used in our previous works for the chelatometric radiometric titration of zinc [6, 8], cobalt [7, 9, 12] and B_{12} vitamine [10, 11]. These titrations were done by EDTA and DCYTA titrants, liquid, solid ion exchangers, and ion exchanger membranes were used for the separation of components.

In the present paper results obtained in the radiometric titration of Fe^{3+} ions labelled with $^{55+59}Fe$ using EDTA titrant are reported. For the separation of components *DOWEX 50 W—X2* was used. In this way iron was determined in pharmaceutical iron tincture *(Tinctura aromatica)* in amounts of tenths of per cents. The method developed can be also used for the determination of iron in submicro quantities. The determination of greater quantities of iron is also possible, mostly in routine analyses (as in our case, in the serial analysis of pharmaceutical products), where calibration curves are mainly used.

Principle of the method

In the titration of Fe^{3+} ions by EDTA titrant, a negative charged chelate complex is formed

$$Fe^{3+} + H_2Y^{2-} \rightleftharpoons FeY^- + 2\,H^+$$

Non-reacting Fe^{3+} ions are separated from the chelate complex formed during titration by an exchanger. The radioactivity of the chelate complex (solution) is measured.

Although in the determination of Fe^{3+} ions present in concentrations like in the pharmaceutical product Tinctura Ferri aromatica the titration curves can be evaluated and extrapolated up to the end point, it is more advantageous to use a calibration curve. To understand this method we refer to Figs. 1 and 2 where titration and calibration curves obtained in our experiments are shown.

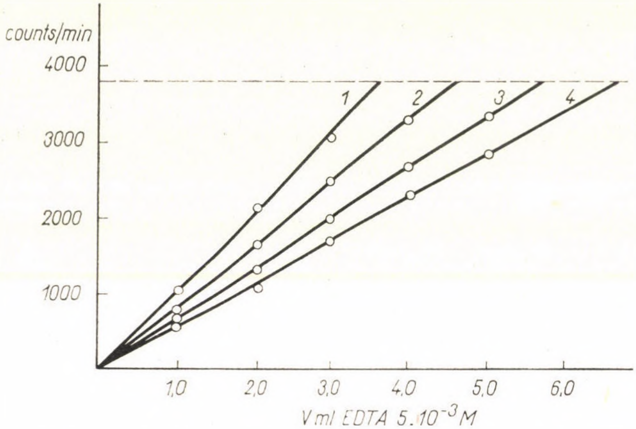

Fig. 1. The relation between different quantities of labelled chelate and the EDTA titrant (1 — indicator; 2 — indicator + 0.28 mg Fe; 3 — indicator + 0.56 mg Fe; 4 — indicator + 0.84 mg Fe)

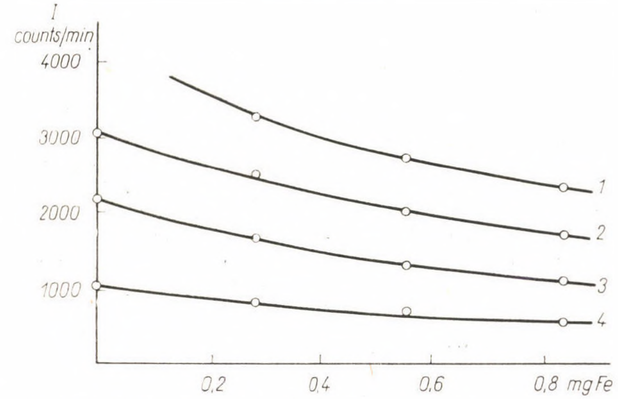

Fig 2. Calibration curves constructed by using the values in Fig. 1 (1 — 4 ml; 2 — 4 ml; 3 — 2 ml; 4 — 1 ml 5 · 10^{-3} M EDTA)

Fig. 1 indicates the relation between the activity of different quantities of labelled chelate ($^{*}FeY^{-}$) and the amount of EDTA added to the investigated solution. Fig. 2 indicates the relation between the activity of labelled chelate and the quantity of iron at constant EDTA titrant volume.

The amount of iron can be determined by the calibration curves shown in Fig. 2 as follows: Always exactly the same amount of radioactive indicator

($^{55+59}$Fe) is added to the solution under investigation. After the addition of definite quantities of EDTA titrant, the separation is done by cation exchanger and the radioactivity of the labelled chelate (solution) is measured. This measured activity is then marked on the y-axis and from its intercept with the calibration curve constructed for the corresponding (added) quantity of titrant a line perpendicular to the x-axis is drawn and gives the sought amount of Fe^{3+}.

Experimental

Reagents, radioactive indicators, ion exchangers and titrants used

All the reagents used were of p. a. grade *(Lachema n. p.)*.

The distilled water used was purified by deionization using *Dovex 50 W—X2* and *Dowex 1—X8* ion exchange mixtures. $^{55+59}$Fe was used as the radioactive indicator. The ion exchanger used for the separation of components was *Dowex 50 W—X2* (100/200 mesh).

Traces of iron and cobalt were removed from the cation exchanger before use as follows: The necessary amount of cation exchanger was washed on the column by 6 N HCl in a thirtyfold excess. Then it was rinsed with deionized water, and carried into Na^+ cycle by 5% NaCl solution. The cation exchanger was treated, after rinsing it with deionized water, by a sixtyfold volume excess of 10% EDTA solution, then by thirtyfold excess of deionized water.

$5 \cdot 10^{-3}$ M EDTA *(Komplexon III)* solution was used as titrant. The solution was standardized bv recrystallized p. a. grade lead chloride using xilenol orange indicator [13].

Construction of calibration curve

To 0.2 ml solution of $^{55+59}$Fe indicator known volumes of a non-active standard iron solution were added then 0.2 ml 30% H_2O_2, and the volume of the solution was completed to 5 ml. The solution was boiled for three minutes in a 25 ml flask equipped with a cooler, it was cooled, and the cooler was washed with 3 ml deionized water. The flask was separated from the cooler, a certain quantity of $5 \cdot 10^{-3}$ M EDTA titrant was added to the solution it was filled up with deionized water to 10 ml, and 200 mg *Dowex 50 W—X2* in Na^+ cycle was added to it. The solution containing the ion exchanger was mixed by air bubbling. Then the ion exchanger was separated from the solution by filtering through filter paper. The ion exchanger on the filter paper was thoroughly rinsed, and the eluate was made up with deionized water to 25 ml. After mixing, the solution was placed into a beaker, then sucked into a GM tube for solution-counting where the activity of the solution was measured. In this way the different points of the titration and calibration curves were obtained.

$(NH_4)_2Fe(SO_4)_2$ solution was used as standard solution. The quantity of iron in the standard solution was determined by gravimetry.

The determination of iron in Tinctura aromatica

In determining iron in aromatic iron tincture the same procedure was used as in the determination of the different points of the calibration curve, with the exception that instead of $(NH_4)_2Fe(SO_4)_2$ standard solution 0.1—0.2 ml of the investigated tincture was added from a micro burette. The amount of iron in the tincture was determined by a calibration curve, as indicated above. Experimental results obtained in radiochelatometric titration were compared to results obtained by iodometric titration [14] prescribed by the pharmacopoea.

Experimental results

The titration and calibration curves are shown in Figs. 1 and 2 obtained by the $(NH_4)_2Fe(SO_4)_2$ standard solution for titration using $5 \cdot 10^{-3}$ M EDTA solution. Experimental results obtained in radiochelatometric and iodometric titrations (the determination of iron in aromatic iron tinctura) are shown in Table I.

Table I

The determination of iron in Tinctura Ferri aromatica

Fe %		Deviation %
Method given in pharmacopoea (iodometric)	Determination by radiochelatometric titration	
0.208	0.210	+0.96
	0.210	+0.96
	0.208	0.00
0.212	0.218	+2.83
	0.212	0.00
	0.210	—0.95
0.210	0.215	+2.38
	0.212	+0.95
	0.210	0.00

Experimental results obtained in radiochelatometric titration show a constant deviation in the positive direction. This is probably caused by the fact that within the given concentration limits of the sample and the titrant the adsorption of EDTA on the dry matter present in the tincture cannot be controlled.

SUMMARY

This paper deals with chelating radiometric titration. $5 \cdot 10^{-3}$ M EDTA solution, *Dowex 50 W—X2* cation exchanger and $^{55+59}$Fe radio nuclide were used as the titrant, for the separation of components, and as the indicator, respectively. The method, the procedure and the results obtained are described in the paper. In this way quantity of iron in pharmaceutical products *(Tinctura Ferri aromatica)* were determined. The method can be used to determine amounts of submicro grams of iron.

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THERMOGRAVIMETRIE UND GLEICHZEITIG LAUFENDE UR-ABSORPTIONSSPEKTROSKOPIE DER GASPHASE

EINE STUDIE ZUR MANGAN(II)-CARBONAT-THERMOLYSE

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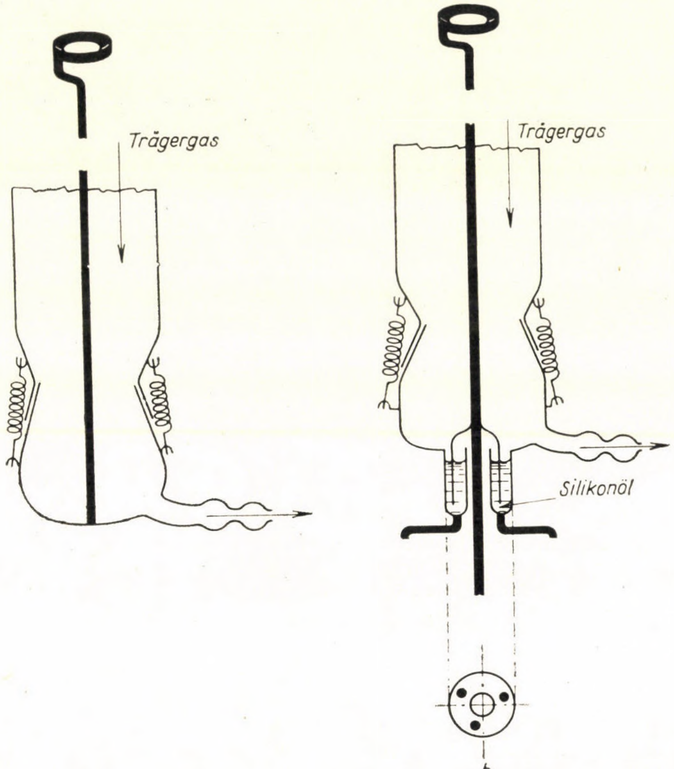
Um genauere Informationen über den Mechanismus der Mangan(II)-carbonat-Thermolyse, ja über thermische Abbauprozesse im allgemeinen einholen zu können, haben wir die Abgase der Zersetzungsreaktion aus dem Reaktionsrohr unserer Chevenardschen Thermowaage, mit Hilfe verschiedener Trägergase, eine möglichst kurze und enge Glas an Glas Verbindung benutzend, unmittelbar durch die 11 cm lange und 250 ml fassende Gasküvette eines *IKSZ-14* UR-Spektrophotometers geleitet, wobei in die Vergleichsküvette das Trägergas allein untergebracht wurde. Falls eine größere Empfindlichkeit nötig ist, so kann man sich natürlich auch einer Durchflußküvette mit wiederholter Reflexion bedienen. Bei der Durchführung der Versuche wurde die untere Austrittsöffnung des Einsatzrohres der Thermowaage mit einem in Abb. 1a skizzierten geschliffenen Quarzglasstopfen, oder mit einem in Abb. 1b entworfenen, zur gleichzeitigen kontinuierlichen Wägung geeigneten Quarzverschluß versehen.

Als erstes untersuchten wir die bekannte mehrmals beschriebene Zersetzung des Mangan(II)-carbonates [1, 2] und erhielten die Kurven in Abb. 2 mit Luft, bzw. die Kurven in Abb. 3 mit hochreinem N_2 als Trägergas. Die UR-Absorption wurde bei $\lambda_{CO_2} = 2349$ cm^{-1} mit einem Papiervorschub von 90 mm/h registriert. Die Strömungsgeschwindigkeit des Trägergases hielten wir mit Hilfe eines kalibrierten Kapillarmanometers und mit einem Präzisionsgasreduktor eines *Zeiss* (Jena) Flammenphotometers genau auf 10 l/h konstant. Da das Spektrophotometer letzten Endes die Konzentration des gasförmigen Zersetzungsproduktes im strömendem Trägergas in der Funktion der Zeit aufzeichnet, werden mit steigenden Strömungsgeschwindigkeiten des Trägergases kleinere Flächen, d. h. in unserem Fall kleinere CO_2-Mengen erhalten. Bei konstanten spektrophotometrischen und thermogravimetrischen Bedingungen ist aber die Menge des gebildeten und mitgeführten Gases direkt der Fläche proportional, die vom Spektrophotometer, infolge der Änderung der CO_2-Konzentration im Trägergas, registriert wird. Auf Grund der planimetrischen



b)

Abb. 1. Verschlüsse zum Einsatzrohr der Chevenardschen Thermowaage

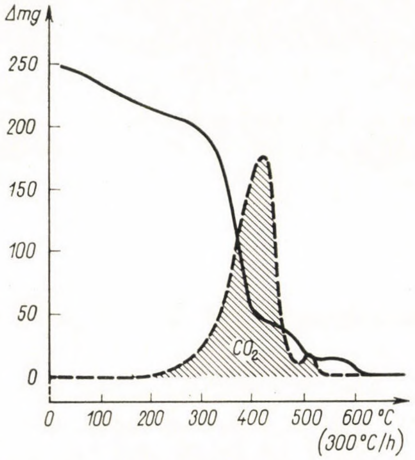


Abb. 2. Gravimetrische Thermokurve der Mangan (II)-carbonat-Thermolyse und das zugehörige UR-Spektrogramm des dabei entstehenden CO_2. Einwaage; 722,1 mg Mn $(CO_3)_{0,881}$ $(OH)_{0,238}$. $(H_2O)_{0,447}$. Zu 233,2 mg gehören 24,3 cm², bei 10 l/h Luft als Trägergas. Endprodukt Mn_2O_3

Auswertung der Original-UR-Spektrogramme erhielten wier 24,3 cm^2 im Falle von Luft und 23,9 cm^2 im Falle von N_2 als Trägergase. Die Differenz dürfte entweder von der Unterschiedlichkeit der inneren Reibungskoeffizienten der beiden Trägergase, oder von der Entstehung von CO bei der Verwendung eines Intergases herrühren. Zur Kontrolle dieser letzterwähnten Möglichkeit haben wir versucht auf gleiche Weise, aber bei $\lambda_{CO} = 2182$ cm^{-1} sowie auch mit doppelter Carbonateinwaage die CO-Konzentration des Trägergases zu erfassen, jedoch erfolglos.

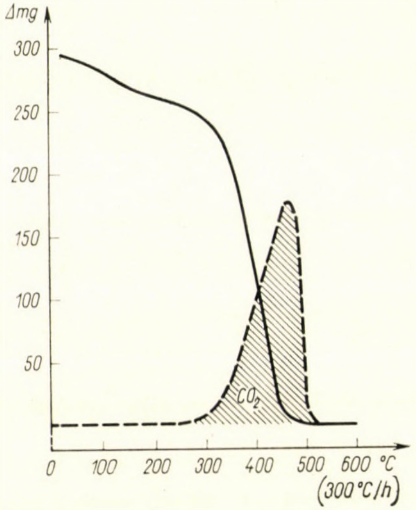


Abb. 3 Gravimetrische Thermokurve der Mangan (II)-carbonat-Thermolyse und das zugehörige UR-Spektrogramm des dabei entstehenden CO_2. Einwaage; 722,3 mg $Mn(CO_3)_{0,881}(OH)_{0,238} \cdot (H_2O)_{0,447}$. Zu 233,3 mg CO_2 gehören 23,9 cm^2, bei 10 l/h Stickstoff als Trägergas. Endprodukt MnO

Die erhaltenen Kurven scheinen von den beiden in einer früheren Arbeit [1] vertretenen Annahmen diejenige zu bekräftigen, nach welcher bei der Zersetzung in Luft zuerst MnO entsteht, das durch den Luftsauerstoff zu MnO_2 oxydiert wird. Die somit zustandegekommene MnO_2-Deckschicht verhindert besonders bei den größeren Körnchen die CO_2- und O_2-Diffusion und bremst dadurch die Geschwindigkeit der Reaktion beträchtlich ab. Mit steigende, Temperatur wird aber die Deckschicht durch den CO_2-Überdruck aufgerissenr so daß die Thermolyse weiterlaufen kann, und es entsteht als Folge dieser Geschehnisse das kleine CO_2-Absorptionsmaximum in Abb. 2.

Zur Zeit bearbeiten wir mit derselben kombinierten Methode die Thermolyse des Ammoniumwolframates, Ammoniummolybdates, Mangan(II)-oxalates, weiterhin die Pyrolyse des Zinksulfids usw. und werden über unsere neuere Ergebnisse an anderer Stelle berichten.

Hier möchten wir noch Herrn Direktor A. KOMPORDAY für die Genehmigung der Publikation danken.

ZUSAMMENFASSUNG

Dadurch, daß man die im Reaktionsraum der Thermowaage entstandenen gasförmigen Abbauprodukte der Mangan(II)-carbonat-Thermolyse, oder einer Abbaureaktion im allgemeinen, mittels eines strömenden Trägergases unmittelbar durch die Küvette eines UR-Spektrophotometers leitet, und die Absorption bei der Wellenlänge eines geeigneten Absorptionsmaximums des entsprechenden Abbaugases in der Funktion der Zeit bzw. Temperatur einzeln registriert, lassen sich über den Mechanismus der Zersetzungsreaktion weitere wertvolle Informationen einholen.

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ON THE THEORY OF THE CRYSTAL-LIQUID PHASE TRANSITION

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Introduction

The distribution function method $F_s(q_1, q_2, \ldots, q_s)$ $(s = 1, 2, \ldots, N)$ is one of the most effective methods of statistical investigations of many-body systems [1] $\left(\frac{1}{V_s} \cdot F_s(q_1, q_2,, \ldots, q_s\right) dq_1\, dq_2 \ldots dq_s$ is the probability that s given molecules are near to the point with given coordinates (the Cartesian coordinates of vector q are q^α, where $\alpha = 1, 2, 3$); N is the number of particles of the system in volume V).

The functions $F(q_1, q_2, \ldots, q_s)$ are interrelated by the BOGOLYUBOV—BORN—GREEN's series of equations.

The first equation of this series — the equation for unitary distribution function $F_1(q)$ is:

$$\Theta \frac{\partial F_1(q)}{\partial q^\alpha} + \frac{1}{v} \int \frac{\partial \Phi(|q-q'|)}{\partial q^\alpha} F_2(q,q')\, dq' = 0 \tag{1}$$

($\Theta = kT$, $T =$ absolute temperature, $v = \frac{V}{N}$, $\Phi(|q|) =$ interaction potential between pairs of particles).

Solution of the Equation (1) is not possible, because it contains the unknown pair distribution function too $F_2(q, q')$ except $F_1(q)$. To split the BOGOLYUBOV—BORN—GREEN's series equations we take

$$F_2(q, q') = F_1(q)\, F_1(q') \tag{2}$$

Then we obtain for the density (number of particles) $\varrho(q) = \frac{1}{v} F_1(q)$ the closed equation with self-consistent field:

$$\Theta \ln \lambda \varrho(q) + \int \Phi(|q - q'|)\, \varrho(q')\, dq' = 0\,, \tag{3}$$

where λ normalization constant; $\int \Phi(|q - q'|)\, \varrho(q')\, dq' = \mu(q) =$ the self-consistent potential.

Equation (3) was first applied to a crystal by A. A. VLASOV [2]. This application was sharply criticized by several authors [3, 4, 5]. These authors attempted to prove the inapplicability of Equation (3) to a crystal [3, 4, 5]. However, Equation (3) is shown to be a good approximation for a crystal and gives qualitatively good results for the liquid and gas phases (these results are good quantitatively also within the order of magnitude) [6, 7].

In [6] the solution of the non-linear Equation (3) was reduced to the variational problem on the minimum of a functional depending on the self-consistent potential $\mu(q)$ for the free energy of the system $F(n)$.

Since Equation (3) under some circumstances has one spatially homogenous solution and one periodical solution for the density $\varrho(q)$, the possibility is suggested for the calculation of the free energy for the liquid phase and for the crystal phase with the help of the functional $F(n)$. It should render possible to develop the consequent theory of the crystal-liquid phase transition (in the approximation of the self-consistent field) under the assumption that these phases coexist simultaneously and have the same chemical potentials, temperatures and pressures.

Free energies of the liquid and the crystal

According to [7] the free energy per molecule in the liquid phase is

$$f' = -\Theta \ln e v' + \frac{2F_1}{v'} \cdot I, \tag{4}$$

where v' the volume per particle of the liquid, $I = \int\limits_d^\infty \Phi(r) r^2 \, dr$, d — is the parameter of cut-off of the potential at the small distances (which depends on the property of the liquid: see [7], e is the NEPER's number.

If one takes $\Phi(r)$ to be the LENNARD—JONES potential

$$\Phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

the following equation is obtained for the free energy of a crystal [6]:

$$F = 3N\Theta \ln \omega +$$

$$+ \frac{N z \varepsilon \sigma^2 \omega^3}{4\Theta a} \sqrt{\frac{m}{F_1 \Theta}} \int\limits_0^{2b} A(x) e^{-\frac{m\omega^2 x^2}{\Theta}} x \, dx + F_0, \tag{5}$$

where

$$A(x) = \frac{1}{5}\left[\left(\frac{\sigma}{x-a}\right)^{10} - \left(\frac{\sigma}{x+a}\right)^{10}\right] - \frac{1}{2}\left[\left(\frac{\sigma}{x-a}\right)^{4} - \left(\frac{\sigma}{x+a}\right)^{4}\right],$$

$$F_0 = -\frac{3}{2} N\Theta \left(1 + \ln \frac{2F_1\Theta}{m}\right],$$

Z is the number of the nearest neighbours in the crystal, a, b and ω are the variational parameters (a is the distance between the nearest molecules, b determines the region of movement in the crystal lattice for the molecule of mass m).

Eq. (5) will be the best value of the free energy of the crystal, if the variational parameters are determined by the minimization conditions:

$$\frac{\partial F}{\partial \omega} = 0, \qquad \frac{\partial F}{\partial a} = 0, \qquad \frac{\partial F}{\partial b} = 0 \tag{6}$$

The second expression corresponds to the external pressure $p = 0$; this assumption is rather good for the crystal under pressures below a few atmospheres. If one takes into consideration the external pressure the value of the parameter a will be obtained from the following condition [8].

$$p = -\frac{a}{3v} \cdot \frac{\partial f}{\partial a}$$

$$\left(f = \frac{F}{N}\right) \tag{7}$$

The third of the conditions (6) gives $b = 0{,}1\,a$ for the region of the vibration of molecule in the crystal of inert gases around the equilibrium position.

The melting theory and "the rule of the half"

To determine the melting temperature and its dependence on the pressure one has to assume the equality of the chemical potentials of the crystal and liquid phases.

Letters describing the liquid phase values are underlined. Letters without underlining refer to the crystal phase. During the melting process

$$\mu(T, p) = \mu'(T, p)$$

or

$$f'(T, v') - f(T, v) = p \cdot (v - v'), \tag{8}$$

where values of v and of v' can be calculated as functions of p and T from the equations as such:

$$p = -\frac{\partial f}{\partial v} = -\frac{\partial f'}{\partial v'} \tag{9}$$

Usually it can be assumed that $p = 0$ (it is valid for pressures below a few atmospheres), therefore Eq. (8) is reduced to the following one:

$$f(T, v) = f'(T, v') . \tag{10}$$

Substituting f' from (4) and f from (5) and solving the obtained equation under the conditions (6), one can obtain the melting temperature T_m for the crystals of the VAN DER WAALS type. The obtained values of T_m fit the experimental data (see Table I).

Table I

Substance	T_m calculated	T_m^{exp} experimental
Ar	65	83
Ne	19	24
Kr	80	116
Xe	126	161

From our point of view the small discrepancy between T_m and T_m^{exp} is due to the model nature of the LENNARD—JONES potential.

With the help of (4) and (5) one can also calculate the changes of volume $\triangle V = V' - V$ and changes of entropy $\triangle S = S' - S$ during the process of melting for the crystals of VAN DER WAALS type.

In the case of crystals the condition $\frac{\partial f}{\partial v} = 0$ or Eq. (7) determines the value of the parameter a, in the case of liquids the conditions $p = -\frac{\partial f'}{\partial v'} = 0$ makes it possible to obtain the relation between the melting temperature and the critical temperature for all substances with the critical pressure below 50 atmosphere.

In fact, it is found that

$$\Theta_m = -2\pi \varrho_m I_0 \tag{11}$$

from Eq. (4) for the process of melting under the condition $p = 0$, where ϱ_m is the density of the liquid at the melting temperature $\Theta_m = kT_m$.

On the other hand, according to [7]

$$\Theta_c = -4\Pi_1 \varrho_c I_1 \tag{12}$$

where Θ_c and ϱ_c are the corresponding critical temperature (expressed in energy units) and density, I_1 is the magnitude of I at the critical point.

One can obtain from Eq. (11) and Eq. (12)

$$T_m = \frac{1}{2} \cdot T_c \cdot \frac{\varrho_m \cdot I_0}{\varrho_c \cdot I_1} . \tag{13}$$

From Eq. (13) it is also obtained that

$$T_m = \frac{1}{2} \cdot T_c \tag{14}$$

assuming that the ratio $\frac{I_0}{I_1}$ is opposite to that of the corresponding densities $\left(\frac{I_0}{I_1} = \frac{\varrho_c}{\varrho_m}\right)$.

Table II confirms the validity of this equation (and simultaneously that of the assumption made for the value of the ratio of the values of the integrals). This table contains the experimental data on the melting temperatures (at atmospheric pressure) and the halves of the critical temperatures for several substances in the order of rising critical pressure from 12.8 atm (for hydrogen) up to 46 atm (for methane).

Table II

Substance	T_m	$\frac{1}{2} T_c$
H_2	16	16.5
Ne	24.4	22.5
N	63	63
CO	68	67.2
CH_4	91	95

One can see from the Table II that Eq. (14) provides approximations of large precision for all substances having critical pressure below 46 atm.

We call this relation between the melting temperature and "critical" temperature as "the rule of the half".

In theory recently this rule has not been known; it may be obtained only with the help of the self-consistent field method. It is important to remark that this rule is obtained without any information about the interaction law for the molecules of the crystal.

This fact is very important since this interaction law is not known sufficiently well at the present time.

The Author would like to express his sincere thanks to Academician N. N. Bogolyubov for fruitful discussions about this paper.

SUMMARY

A consequent statistical theory of melting has been developed in the approximation of the self-consistent field; it is based on the equality of the chemical potentials of crystal phase and liquid phase coexisting simultaneously. The melting temperatures derived for the crystals of inert gases are in agreement with the experimental data. Moreover "the rule of the half" has been derived according to which the melting temperature (at about atmospheric pressure) is equal to half of the critical temperature for all substances with a critical pressure below 50 atmospheres.

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THE MECHANISM OF VAPOUR ADSORPTION, I

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Introduction

Theoretical considerations aimed at describing vapour adsorption isotherms, as well as the models used for this purpose, assume, in general, ideal surfaces. The ideal character is reflected by two properties of these models: they are energetically homogeneous surfaces, or they have a certain energy distribution assumed to be known, and they are geometrically plane surfaces. The BET isotherm, used most frequently for the calculation of the specific surface of actual adsorbents, is based on similar assumptions. However, in reality adsorbents generally differ from these idealized models, or it takes rather great circumspection and efforts to produce surfaces corresponding to such models. These materials are then unsuitable for practical purposes.

In the present work we report on experiments undertaken with the object to follow the development of adsorption layers built up during vapour adsorption on real surfaces, that is to say, on surfaces which cannot be considered ideal either from the energetical or from the geometrical point of view.

The experimental method was essentially equilibration of the adsorbent with a vapour of given pressure, and while maintaining the partial equilibrium pressure of the vapour in the gaseous phase, the adsorbent was contacted with another gaseous adsorptive. The relative pressures of the two adsorptives differed to such an extent that no desorption of the first upon the action of the second was practically observed; the first adsorbate could be considered a liquid, and the second a gas.

The second adsorptive may be bound in four different ways on the surface that has been covered by the first adsorptive: (a) dissolution in the first adsorptive which is regarded as a liquid; (b) adsorption at the liquid-gas interface (on the surface of the first liquid adsorptive); (c) adsorption at the liquid-solid interface (at the interface of the first adsorptive and the adsorbent); (d) adsorption at the solid-gas interface, if, for some reason, the first adsorptive liquid does not cover completely the surface of the adsorbent.

In reality, most probably all four actions cooperate in the binding of the second adsorptive. An analysis of the experimental results shows, however, that of these four actions only the role of the last is of importance.

The discussed experiment can be actually considered as a measurement of gas solubility: the apparent solubility of the second adsorptive (the gas) has to be measured in the first adsorptive (liquid) fixed on the surface. The difference between the solubility measured in the free liquid (first adsorptive) and the obtained apparent solubility will be the value which is to be evaluated.

In our first experimental series dynamic methods were used: the technique and results have been reported [1]. In our further work static measuring methods were employed. Also here, various silica gels served as the adsorbent, acetone was used as the first adsorptive, and CO_2 as the second adsorptive.

Measuring techniques

A simple volumetric BET apparatus was employed as the measuring equipment. Only CO_2 was measured volumetrically, the adsorbed quantity of acetone was determined by weighing. A trap connected to a conduct pipe served for the feeding of acetone, the primary adsorptive, which was evaporated from this trap into the apparatus. In view of the static measuring method, CO_2 had to be purified thoroughly. This was accomplished by sublimation and by vigorous suction of the solid CO_2.

The measurements were carried out as follows: After the determination of the dead space (at room temperature with H_2) and after measuring the surface by means of nitrogen-adsorption, the adsorbent was heated again and degassed by sucking: it was then contacted with acetone of known partial pressure until equilibrium was attained. Attaining of the equilibrium was indicated by the constancy of pressure in the system shut off from the acetone trap, and by the constant weight of the adsorbent. The measurements were made at 30 ± 0.1 °C. Acetone condensation occurring while weighing the adsorbent vessel (the balance was always in a room of a temperature lower than 30°C) was taken into consideration by effecting a slight desorption after weighing.

After the equilibrium adsorption of acetone had been attained, CO_2 was contacted with the adsorbent, and with the acetone fixed on it, by two methods.

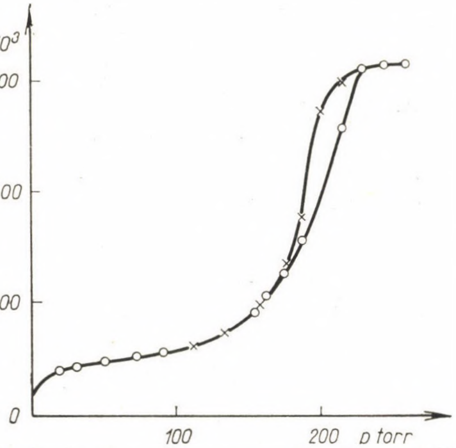

Fig. 1. Acetone isoterm on silica S_1 at 30 °C

1. The stopcock of the adsorbent vessel was closed, and CO_2 of a pressure read on the manometer was introduced into the acetone vapour, this pressure corresponding to the equilibrium vapour pressure of acetone prevailing in the other parts of the apparatus. When the

stopcock, of the adsorbent vessel was opened, CO_2 was bound on the adsorbent-acetone system while the vapour pressure of acetone remained unchanged. This method is very exact, however, it has the disadvantage that even in the useful space of the apparatus the homogeneous distribution of acetone vapour and CO_2 is attained very slowly, moreover, diffusion of CO_2 to the adsorbent is very slow through the conduct pipe of relatively small diameter.

2. After attaining equilibrium acetone absorption, the vessel holding the adsorbent was shut off, the other parts of the apparatus were evacuated and filled with CO_2 of known pressure. On opening the stopcock of the adsorbent vessel, CO_2 entered, and equilibrium was attained with the adsorbent-acetone system. During the inflow of CO_2, no acetone can escape by diffusion, since in the narrow pipe it is pushed back by the stream of CO_2. As soon as the manometer has ceased to fall, the attainment of "equilibrium" has to be observed immediately, since afterwards acetone may escape by diffusion. Whether this has happened or not may be checked by a control measurement described in [1], by comparison of the amount of adsorbed, calculated from its volume, with the result of weighing. Preliminary tests showed that the second procedure if due caution is observed, gives results completely in agreement with those of the first method, in a much shorter time. Therefore, the second technique was used during the following investigations. It should be noted that here actually only the adsorption and dissolution equilibria were established in the adsorbent vessel, but this was the very object of the investigation; the concentrations did not become uniform between the vapour space of the vessel and the remaining space of the apparatus: the total pressure (CO_2 + acetone) prevailing in the adsorbent vessel was equal to the partial pressure of CO_2 in the other parts of the apparatus. Therefore, in the volumetric calculations the CO_2 pressures read on the manometer had to be taken into account, while the equilibrium pressure of CO_2 adsorption was given by the difference between the second CO_2 pressure and the equilibrium pressure of acetone vapour (the equilibrium pressure of CO_2 prevailing in the adsorbent vessel).

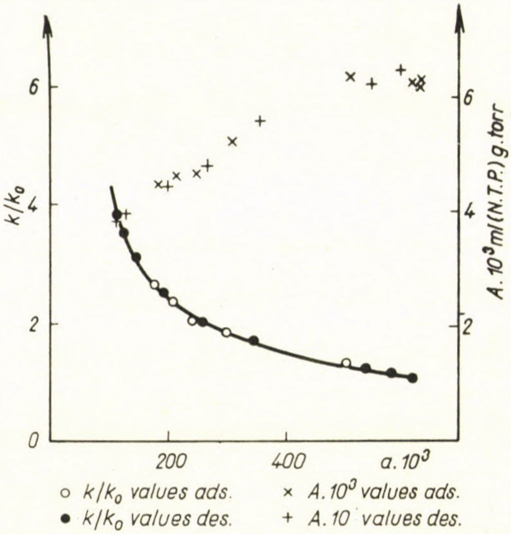

Fig. 2. Acetone-CO_2 system on silica S_1 at 30°C

In contrast to the previous (dynamic) measurements, in this measuring series and in those described below, the adsorption of CO_2 on the adsorbent-acetone system was determined not only at a single CO_2 pressure, but a CO_2 isotherm consisting of several points has been plotted for each case of acetone-adsorbent equilibria. This was done because the nature of the CO_2 isotherm was of interest, moreover, we wanted to increase hereby the measuring accuracy. All CO_2-isotherms were found to be linear within the experimental error. Therefore, this extension of our measuring program served only to increase the accuracy; in the few cases when the points of the CO_2-isotherm showed scattering, the apparent solubility was calculated from the straight line fitted to these points. However, such cases were rather infrequent. The linearity of the sorption of CO_2 justifies the characterization of this sorption by a single value. It follows from the method that even the lowest initial CO_2 pressure was higher than the equilibrium acetone pressure. The CO_2-isotherm at 30°C was also determined on the adsorbent.

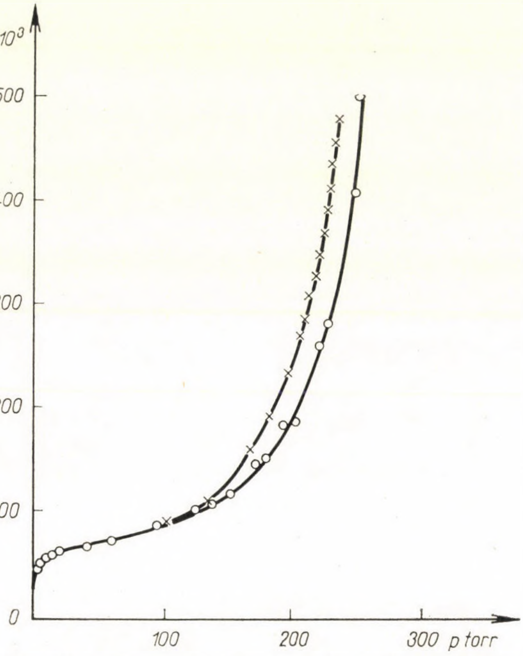

Fig. 3. Acetone isotherm on silica S_2 at 30°C

The apparent solubilities have been characterized by the solubility coefficient:

k (n ml of gas/g of solvent · equilibrium gas pressure in torr)

The k/k_0 value plotted on the diagrams is the ratio of the measured apparent solubility coefficient and the coefficient (k_0) pertaining to the free liquid. The value of A is proportional to the quantity of gas bound by 1 g of the adsorbent:

A (n ml of gas/g of adsorbent · torr) = $k \cdot a$, where a is the number of grams of the first adsorbate on 1 g of the adsorbent.

The results of the measurements are presented in Figs. 1—10 and Table I. Notations in the figures are the same as above.

Table I

*Solubility and adsorption coefficients of CO_2**

acetone		S_1S	S_2Sz	T	Sz
$k_0 \cdot 10^2$	0.94**	—	—	—	—
$A_0 \cdot 10^2$	—	1.87	1.57	1.37	3.8

* k_0 n ml of CO_2/g of solvent · torr equilibrium pressure
A_0 n ml of CO_2/g of adsorbent · torr equilibrium pressure

** SCHAY, G., SZÉKELY, GY., RÁCZ, GY., TRAPLY, G.: Periodica Polytechn. **2**, 1 (1958)

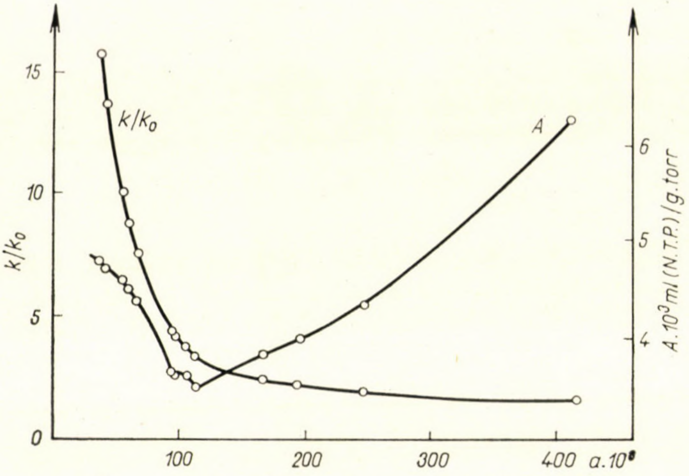

Fig. 4. Acetone-CO$_2$ system on silica S$_2$ at 30°C

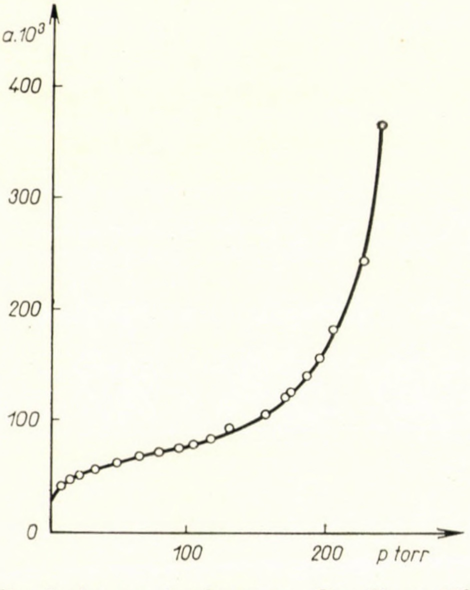

Fig. 5. Acetone isotherm on silica T$_1$ at 30°C

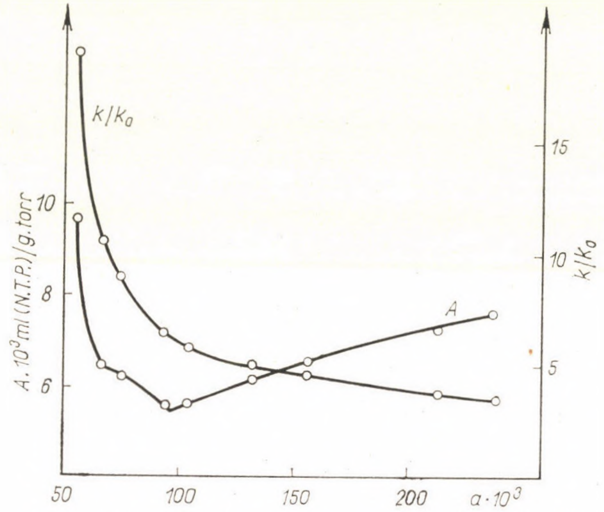

Fig. 6. Acetone-CO_2 system on silica T_2 at 30 °C

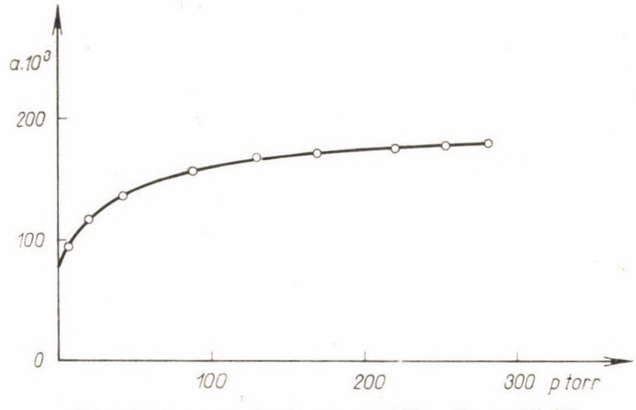

Fig. 7. Acetone isotherm on silica Sz at 30 °C

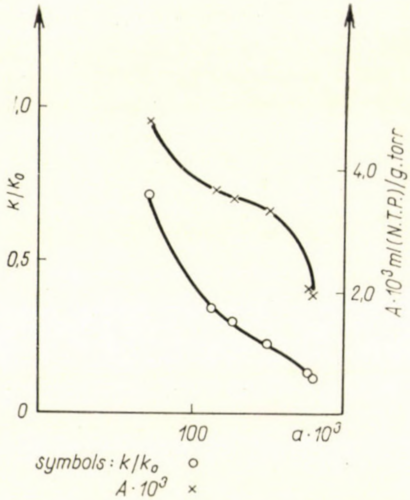

Fig. 8. Acetone-CO_2 system on silica Sz, at 30°C

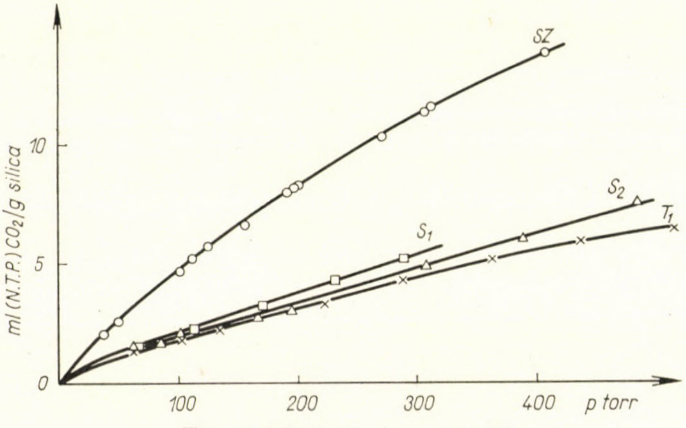

Fig. 9. CO_2 isotherms at 30 °C

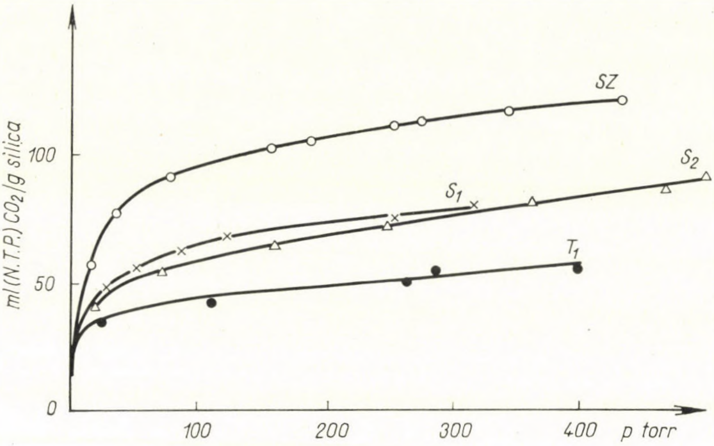

Fig. 10. N_2 isotherms at −183°C

Discussion and interpretation of the results

The chief characteristics of the experimental results may be summarized as follows:*

1. On silica gel adsorbents with wide pores, the apparent solubility is higher than in free acetone along the whole acetone isotherm ($k/k_0 > 1$).

2. On the silica gel with narrow pores, the apparent solubility is lower than the normal solubility (measured in the liquid) along the whole measured section of the acetone isotherm ($k/k_0 < 1$).

3. On adsorbents with wide pores, the value of A (the adsorbed quantity of the second adsorptive referred to unit quantity of the adsorbent) passes through a minimum as the quantity of it is increased.

4. On the adsorbent with narrow pores, the value of A decreases monotonously with increasing the quantity of acetone.

The most remarkable and unexpected feature is the high apparent solubility found on wide pore silica gels, particularly along the inflected sections

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* The following adsorbents were used:

Symbol	Specific surface area, m²/g	Type
S_1	322	mixed pores
S_2	276	wide pores
T_1	210	wide pores
Sz	452	narrow pores

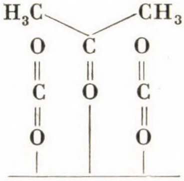
of the acetone isotherms, that is to say, when the nominal monomolecular layers has already been completed. First, this phenomenon will be dealt with, and its interpretation will elucidate also the other three characteristic findings.

The effect may be produced by the four kinds of adsorption processes, mentioned in the introduction, each of which shall be discussed in turn.

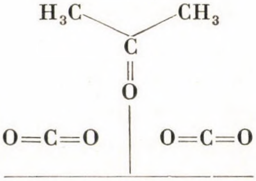
(a) The adsorbed vapour is usually considered a liquid under pressure [2]. This concept appears to be justified also on the basis of the recent measurements, though the method of density measurement with helium has been criticized [3]. Melting point determinations showed without exception that the adsorbate had a lower melting point than the same substance in the free state [4—9]. Even disregarding the inferences to be drawn from the integral enthropy change of adsorption [10, 11], application of infrared spectroscopy to adsorption systems [11, 12, 13] had led to the conclusion that as a result of physical adsorption the adsorbed molecula is generally subjected to similar stresses and distorsions as in solution. Accordingly in a liquid in the adsorbed state, decreased solubilities are to be expected as compared to the free liquid. Nevertheless, to complete this train of thought, let us assume that gas solubility in the adsorbed liquid is higher than normal. In this case, the high values of k and their monotonous decrease with increasing covering of the surface could be explained, since in the upper adsorbed layers solubility would decrease to approach the value measured in the free liquid; the observed monotonous increase in the total adsorbed quantity of gas could also be interpreted. However, as it has been mentioned, on adsorbents of wide pores the total adsorbed quantity first decreases, and after passing through a minimum, it increases. On the other hand, the steep decrease of the k values along the moderately sloping section of the isotherm cannot be explained by this assumption, in fact, it is contrary to experience. Finally this assumption is definitely inconsistent with the experimental results obtained on adsorbents of narrow pores, which indicate, in accordance with expectation, a much lower solubility of the gas in the adsorbed liquid than in the free liquid.

(b) Gas adsorption on the boundary of the first adsorptive, regarded as a liquid, is a problem encountered in the practice of partition gas chromatography, and such effect has actually been readily observed [14]. However, these observations apply to liquids of practically no vapour pressure and of relatively high surface tension, that are hardly comparable with adsorbed acetone. On examining the course of the k/k_0 curves, this assumption must also be rejected. According to present views, the surface area of the adsorbed layer does change along the relatively gently sloping section before the second steep rise of the acetone isotherm, and it is practically the same as the surface area of the adsorbent [15]. A strong decrease of the surface area of the adsorbed layer occurs along the section of the hysteresis loop where it becomes practically zero. **Kiselyov** has calculated the surface area of the adsorbent or, what is practically the same, the area of the adsorbed layer, from the work of this decrease. Independently of the correctness of this method, it is very probable that the surface area of the adsorbate remains almost constant along the nearly horizontal part of the isotherm preceding the second rising section, while it decreases very strongly in the hysteresis section. As contrary to this, the k/k_0 values decrease very steeply in just this horizontal section, and change but very slightly along the hysteresis loop. Finally, the unequivocal dependence of the fixed quantity of acetone, and the identity of the k values measured on the two branches of the hysteresis loop conclusively disprove this assumption, because according to any hysteresis theory, the surface of the adsorbed layer must be different along the two branches (this does not mean, however, that the uncovered surface of the adsorbent must also be different).

(c) This assumption is of itself improbable, because it is difficult to conceive that a solid surface occupied by a molecule is capable for further sorption. The probability should perhaps be considered that some special oriented adsorption of the acetone molecule may permit CO_2 adsorption. This could be represented as follows:



or



Apart from steric reasons, models of this kind must be rejected, because they give no satisfactory explanation for the steep decrease of k on the gently sloping section of the isotherm, or for the levelling out of the decrease in the following section.

(d) There are two possibilities how the adsorbent that has been covered with acetone may have free surface sites suitable for the adsorption of CO_2: one of these is the capillary filter effect; the other, the uneven distribution of acetone permitting the presence of unoccupied sites even at relatively high nominal coverages.

If the observed high adsorption of CO_2 were due to capillaries inaccessible to acetone, the CO_2 fixed in such capillaries would contribute by a constant amount to the total adsorbed quantity. With increasing acetone covering the value of k would decrease, since it would be referred to an increasing quantity of acetone. At the same time, the quantity of fixed CO_2, calculated for the unit quantity of the adsorbent, would continuously increase, because CO_2 would be more or less dissolved by the increasing quantity of acetone; in other words, the value of A would monotonously increase. However, apart from the silica gel S_1, on adsorbents with wide pores, the value of A passes through a minimum, and the fact this was not observed in the case of the silica gel S_1 is due only to the narrow measuring range: with this adsorbent, dynamic measurings began only at higher acetone coverings, and the range of decrease of A falls into the domain of lower acetone coverings. The passing of the value of A through a minimum contradicts the assumption of a capillary filtering effect. Two other facts are also inconsistent with this supposition. The acetone isotherms present, in general, a shape in which the second steep rise (which is usually considered indicative of the development of a polymolecular adsorption layer) is found in the ranges of covering corresponding approximately to the surface calculated from the adsorption N_2; that means, the pores accessible to N_2 are roughly accessible also to acetone. Moreover, the value of k shows a rapid decrease just along that mildly sloping section (after the elbow) of the acetone isotherm where a relatively small change in the quantity of acetone produces great changes of k; at the same time, the value of k decreases but slightly along the second steep section of the acetone isotherm.

The most probable assumption, the only one in accordance with the experimental results, is that after the adsorption of acetone free, uncovered sites are left over on the surface along the isotherm. The gradual disappearance of these sites, their occupation by acetone causes the decrease of k, while the increasing amount of CO_2 dissolved by the adsorbed acetone is expressed by the increase of the total quantity of CO_2 along the isotherm section measured in our experiments. It is assumed that (a) practically no CO_2 has been adsorbed on the surface occupied by acetone, and (b) the solubility of CO_2 in the adsorbed acetone is equal to or less than normal solubility.

The value of k decreases more steeply along the mildly sloping section, because on this part of the isotherm (in accordance also with the BET theory) the unoccupied surface area is relatively large, and this is markedly decreased by the small quantities of adsorbed acetone. Along the steeply rising section of the isotherm, the greatest part of the surface is already covered by acetone, and further increase of its quantity is brought about, instead of adsorption on still uncovered surfaces, by the building up of multilayers on areas covered at least by a monomolecular layer (capillary condensation in the pores).

It follows from this explanation that unoccupied sites are to be found on the surface along the whole measured section of the isotherm. According to measurements carried out on a gel with narrow pores (Fig. 8), the solubility of the gas in the adsorbed acetone is very low. Thus, even if k/k_0 attains unit value along the isotherm (Fig. 2), this factor will be still much higher than the quantity resulting from the dissolution in the adsorbed acetone alone.

Accordingly, the area of the still uncovered surface will decrease rapidly on the gently sloping section of the isotherm. This may be brought about in several ways. It may occur simply by the increase in density of the two-dimensional gas (vapour), or by the increase of the area of the two-dimensional liquid islands, or possibly by the extension of liquid islands of greater thickness. In view of the fact that two-dimensional condensation has been observed, in general, at considerably lower relative pressures [3] (0.03), it would seem reasonable to assume that at the points within the measuring range there are at least two-dimensional liquid islands, and besides these islands and in equilibrium with them, two-dimensional vapour is also present on the surface. Still, a subsequent, more quantitative evaluation of the measurements showed that this concept, too, is erroneous as it also follows from a simple comparison of the results. The binding of a further small quantity of acetone along the gently sloping section of the isotherm results in a strong decrease of k. This is possible only if the binding of this small quantity causes a considerable decrease of the still uncovered surface. However, simultaneously the total quantity of adsorbed CO_2 begins to increase, and this is possible only if at some of the sites the acetone layer is thick enough to dissolve substantial quantities of CO_2. Thus, instead of the surface model covered by a two-dimensional liquid, it is reasonable to consider a model of gradually filling capillaries, or even more, in accordance with the suggestion of PIERCE [15, 16, 17], the formation at the most active sites of liquid islands thicker than two-dimensional, which subsequently extend or merge into one another.

Results obtained on the adsorbent with narrow pores differ also quantitatively from those measured on adsorbents with wide pores. The most remarkable are the very small k/k_0 values, remaining lower than the unit, the plotting of which on a $k/k_0 - a$ curve does not show the bend (elbow) observed in the case of silica with wide pores; moreover, the curve $A - a$ decreases monotonously, also as contrary to previous measurements. At the same time, the steep downward bend before the last smallest values may be seen also in this curve; on curves plotted for adsorbents with wide pores, this characteristic occurs before the minimum.

These results are in full agreement with the model following from what has been said above. The small k and k/k_0 values indicate that on the silica gel with narrow pores, free sites on the surface are by far less, even along the first bend of the isotherm, than were present in the previously discussed case. The uncovered surface sites still present decrease continuously along the higher sections of the isotherm, and the adsorption of CO_2 becomes practically zero well before $p_r = 1$. This means at the same time, that also the acetone present in the pores dissolves but very small amounts of CO_2. The static measuring method permitted to determine the equilibrium from the time dependence of the adsorption of CO_2. Care was taken to allow time for a possible slow diffusion of CO_2 into the narrow pores. However, such effect did not play a part even after the elapse of several hours, so that obtained results were accepted as equilibrium data. From foregoing it is clear why the total quantity of adsorbed

CO_2 does not increase: its solubility in the acetone sorbed in the narrow pores is very little.

On the basis of these results, it can be stated with high probability that uncovered sites are present on the surface of wide-pore silica gels even at relatively high nominal acetone precovering. On the investigated adsorbents with wide pores, the decrease in free surface area is not uniform with the increase of precovering: first, this decrease is steep, to become then mildly sloping along the higher sections of the precoating acetone isotherm.

The area of free surface is much smaller on adsorbents with narrow pores, and the unoccupied sites disappear completely at higher values along the isotherm of the precovering substance.

SUMMARY

The surface of silica gel samples was precovered with acetone, and the quantity of carbon dioxide fixed on such silica gel-acetone systems was measured as the function of the quantity of acetone adsorbed. The results show that on adsorbent samples with wide pores, free surface sites are present even at high acetone coverages, on which the binding of carbon dioxide takes place. On silica gels with narrow pores, there are only few free sites of this kind even at the initial section of the acetone isotherm, to disappear then quickly with the increase in quantity of the covering acetone.

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SOME NEW ASPECTS OF THE MECHANISM OF HYDROGEN EXCHANGE AND HYDROGENATION REACTIONS OVER METAL CATALYSTS

CATALYTIC EXCHANGE REACTION BETWEEN METHANE AND TRITIUM ON Ni CATALYST

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Introduction

Many investigators have used deuterium for studying hydrogen exchange reactions of hydrocarbons over metal catalysts [1—8]. At the beginning of these experiments there was no possibility to determine the different species of deuterized hydrocarbons because of the lack of a convenient experimental method. Later, however, with the help of mass-spectrometer it was established that during the course of this type of reactions more than one hydrogen atom in the hydrocarbon molecule was exchanged for deuterium atoms. According to Kemball [6—8] two mechanisms may be supposed: 1. stepwise and 2. multiple exchange, and at the equilibrium mixture the concentration of different deuterized species can be calculated on a statistical basis.

The main disadvantage of the use of pure deuterium in the catalytic exchange reaction is the occurrence of multiple isotope exchange, *i.e.* it is impossible to study the reaction of only one hydrogen atom in the hydrocarbon molecule. This means that the formation of a hydrocarbon molecule containing one deuterium atom is not independent of that of higher deuterized specimens, whereas in the case of tritium labelled hydrogen the final product is only CH_3T because of the small concentration of tritium. This is the reason why we used hydrogen labelled by tracer amounts of tritium. In addition, the analysis of the products is much easier by means of radioactive counting technique. That is the main reason of this reinvestigation of the exchange reactions between hydrogen and hydrocarbons.

Experimental

Materials

Methane was obtained from a cylinder, and subjected to further purification. First it was dried by passing it through a tube filled with $MgClO_4$. In order to remove all the oxygen, methane passed through manganous oxide heated to 200°C. Finally it was distilled three times under vacuum at liquid nitrogen temperature and was kept in a storage bulb previously evacuated to 10^{-6} Hgmm.

Electrolytic hydrogen was used after purification. This procedure included the removal of oxygen by copper heated to 400°C. The water formed was freezed out at liquid nitrogen temperature in a trap. This hydrogen was stored in a glass bulb.

Hydrogen labelled by tritium was prepared by HORIUTI method [9] using the reaction of metallic sodium with tritiated water having 40 mC/g specific activity. The tritium in hydrogen was present mainly in form of HT and the quantity of T_2 was negligible.

Ni catalyst was used in powder form prepared from $Ni(OH)_2$ by a stream of hydrogen at 400°C. Surface area measured by BET method with N_2 was 4.2 m^2/g.

Apparatus and procedure

The experiments were carried out in all-glass apparatus consisting of two parts shown in Figure 1. The first part (in Figure 1 the left hand side) was the catalytic system itself which contained the reaction vessel connected to a glass circulating pump the iron piston of which was surrounded with an electromagnet controlled by a non-stable multivibrator circuit. By turning stopcocks 1 and 2 the catalytic vessel can be separated from the premixing volume indicated by the dotted lime square. In such a way it was possible to premix the reaction components as well as to analyse the gas mixture before reaction. The volume of catalytic space in which the reaction proceeds was 140 ml. The pressure of the reaction components was measured by mercury manometer read by kathetometer. The catalyst was protected from the mercury vapour by gold leaf.

The reaction vessel was surrounded with an electric furnace controlled by a resistance bridge and amplifier unit. The temperature could be kept within 1% measured by a thermocouple.

The second part (right hand side in Figure 1) was the radio gas chromatographic apparatus. This chromatograph was connected to the catalytic system through the sampling device shown in Figure 2. This allowed one to extract an aliquot which is negligible compared to the whole, but adequate for analysis. In position *a* the sampling stopcock could be evacuated and in position *b* an aliquot could be admitted to it for analysis. By rotating the right hand stopcock through 90° the gas sample could get into the gas chromatograph. The volume of bore (horizontal position in Fig. 2) is 0.134 ml which amounts to 0.1% of the whole reaction system.

The chromatographic column, 80 cm in lenght, was filled with *BDH* Chromatographic Silicagel (40—60 mesh) and it was used at room temperature. Thermal conductivity cells were built into the chromatograph attached to a bridge unit. Since the quantity of the gas sample is very small (a few microliter of gas) the cell was not sensitive enough for quantitative evaluation of the peaks. The output of the bridge therefore was fed into a D. C. amplifier *(Vakutronik Schwingungkondensator Elektrometer type VA—J—51)* for amplifying the bridge current recorded by a pen recorder. Although by using a larger bore in the sampling valve the sensitivity of the thermal conductivity cell could be increased but in this case the radioactivity measurement was uncertain because of the dead time correction.

The radioactivity of the two gases was measured in proportional range by using a flow counter (volume 10 ml) connected through a preamplifier unit (Type *ACEC, PAHG 200)* to an analyser (Type *ACEC, DM 160)*. Purified argon was the carrier gas and just before the counter, methane was fed into the gas stream. The ratio of the two gases was 1 : 9, respectively. Under these circumstances 2700 V was supplied to the counter as optimum high voltage, and the plateau-length was about 300 V. The retention times for hydrogen and methane were 68 and 145 seconds, respectively.

The chromatografic separation and quantitative analysis of the components was achieved under the following conditions. After setting the temperature of the column (25°C), and the flow rate which was 30 $ml \cdot min^{-1}$ for argon and 87 $ml \cdot min^{-1}$ for methane, we measured the background correction during 100 seconds. After admitting the methane-

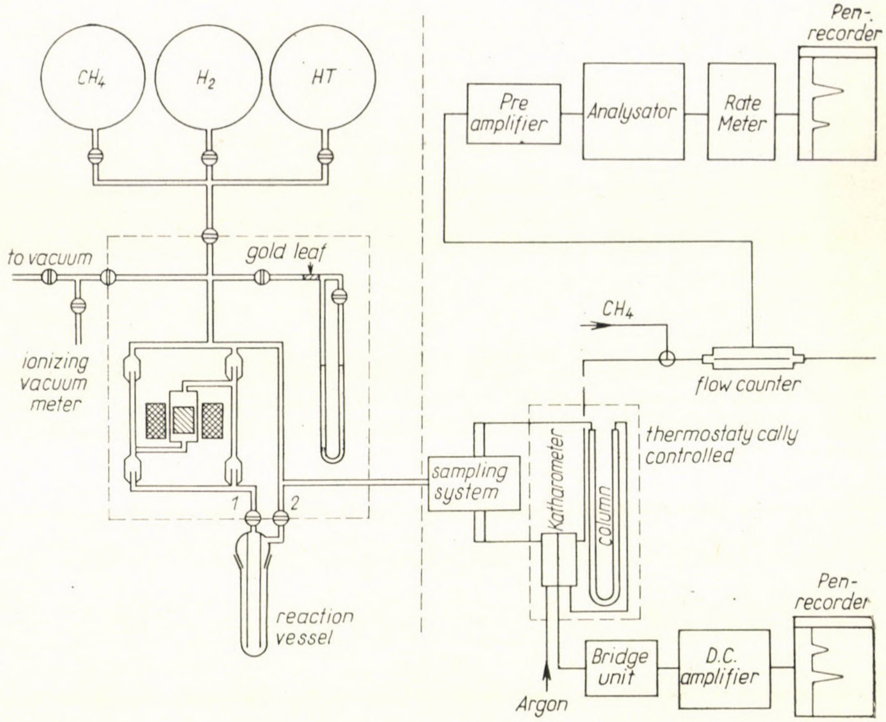

Fig. 1. Sketch of catalytic apparatus and the block diagram for radiochromatograph

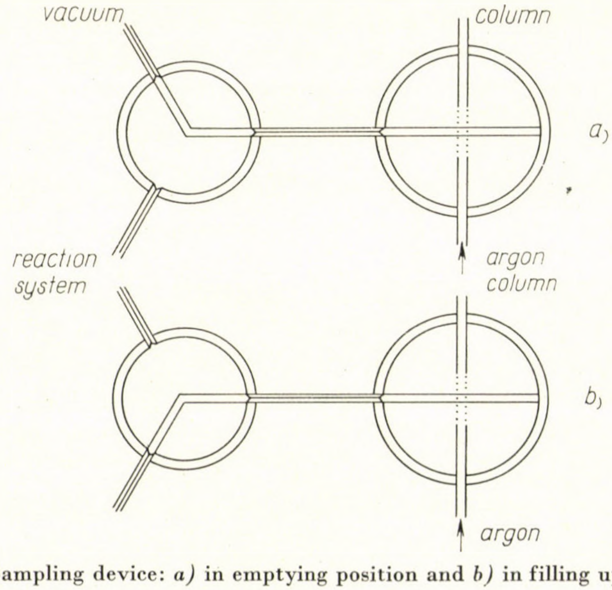

Fig. 2. Sampling device: *a)* in emptying position and *b)* in filling up position

hydrogen mixture to be analysed during the first 100 seconds all the hydrogen in the effluent gas appeared in the counter and during the next 100 seconds, the methane did. Subtracting the background, these counts directly measured the quantities of tritium in form of hydrogen and methane. In such a way it was not necessary to use the ratemeter-penrecorder unit attached to the analyser.

The gas chromatographic system was calibrated by admitting a known amount of hydrogen labelled by tritium. Plotting the tritium disintegrations *versus* the pressure a straigh line, was obtained and it was found that the reproducibility of this procedure within 3%.

The procedure for carrying out an experiment was as follows:

Before and between each experiment the catalyst was pumped off down to 2.5×10^{-5} Hgmm at 250°C, measured by ionizing vacuummeter type *LV—402*. This procedure lasted for one hour and after this treatment the experiments were reproducible within 4%.

A given amount of both gases was admitted into the premixing space and by extracting a small amount out of it the specific radioactivity of tritium labelled hydrogen was measured by gas chromatograph. After this procedure we started the experiment and from time to time we measured the radioactivity of both reaction components. Since there was no change in the mole numbers during the reaction, the radioactivity changes in hydrogen and methane were a direct measure of specific activity and so of the exchange reaction.

Results

The experiments were carried out on Ni catalyst in the temperature interval from 221—256° C at 100 Hgmm over-all pressure. The hydrogen methane ratio was 1 : 1.

Typical runs of the catalytic exchange reaction are shown in Fig. 3 where the percentage exchange calculated from the radioactivity of methane divided by that of methane and hydrogen is plotted against time.

In some experiments carried out up to a higher conversion and at higher temperature, the sum of radioactivity in methane and in hydrogen increased above the value of that present in hydrogen at the beginning of the run. This surprising phenomenon could not be explained by the decrease of counting efficiency of the flow counter resulting from hydrogen because in separate experiments it was established that hydrogen up to 5.4% concentration in the gas stream did not affect the efficiency. At lower temperature and at lower conversion the radioactivity balance was correct within the experimental error.

We assumed therefore that this increment in the overall radioactivity could result from tritium having been remained adsorbed on the catalyst surface in the previous experiments due to a very strong adsorption of tritium at higher temperature.

In order to prove this assumption we plotted some experiments in the following way. For the intersect we put on the values of the ratio of increment in methane radioactivity to the decrement of hydrogen radioactivity for each time interval and for the abscissa the reaction time (Fig. 4) at different temperature. As it is seen this ratio increased very strongly with the increase of temperature.

In order to explain this phenomenon we had two possibilities.

i) Because of the thermodynamic isotope effect the catalyst surface should contain more tritium atoms than the gas phase at the beginning of an experiment. In this case more tritium atoms should enter into methane than disappear from the gas phase, this might lead to an increase in the overall radioactivity. However, equilibrium between the hydrogen in the gas phase and that on the catalyst are very rapidly established. This means for adsorption equilibrium

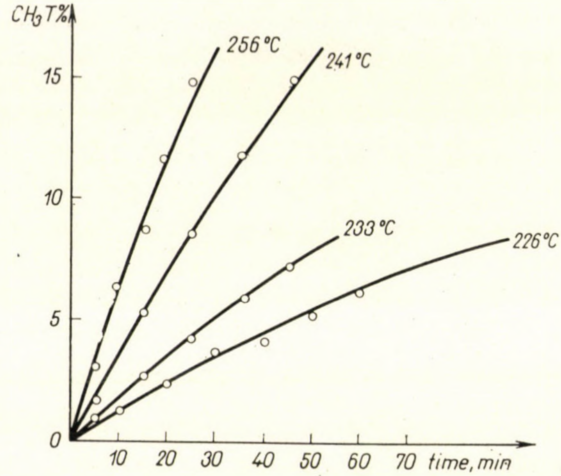

Fig. 3. Typical runs of methane exchange at different temperatures

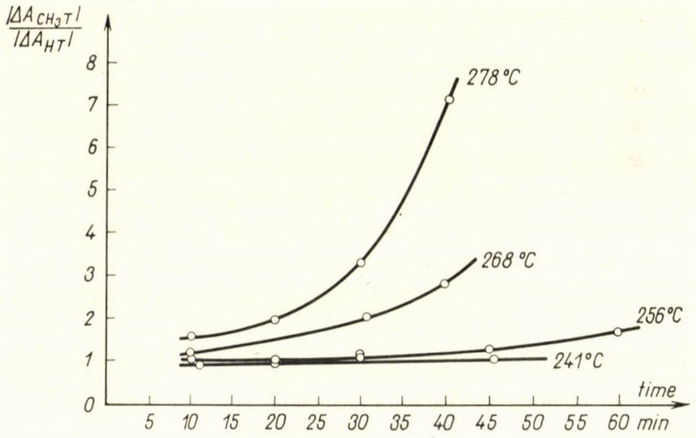

Fig. 4. Ratios of radioactivity appearance in methane for unit time to radioactivity disappearance in hydrogen as a function of time at different temperatures

$$K = \frac{[HT] \text{ surface}}{[HT] \text{ gas}} > 1 \tag{1}$$

therefore in this case the highest amount of tritium enters the methane at the beginning of the run, so the ratio should have the highest value than, and during the course of the reaction it should be constant or decrease.

ii) According to the second possible explanation as the tritium concentration decreases by means of isotope exchange, a new process should be initiated, namely an exchange between the gas-phase hydrogen and the surface tritium. This means that during the run the specific radioactivity of hydrogen should decrease to a smaller extent than the radioactivity of methane increases, which results in an increase both of the over all radioactivity and of the ratio.

The curves in Figure 4 proved that this second explanation is probably valid. However, it was not clarified where this additional radioactivity in the gas phase came from. It was necessary therefore to carry out further experiments by using freshly made catalyst having not been exposed to tritium.

1. On freshly prepared catalyst there was no increase in the total radioactivity of both reaction components even at a higher temperature, but a slight decrease. In the next run, however, we observed these phenomena.

2. In the next experiment after evacuation nonradioactive hydrogen was admitted to the catalyst and an increase was observed in the gas phase radioactivity which meant that between the surface tritium and gas hydrogen an isotopic exchange was taking place.

3. Having carried out the same experiment as in 1., the catalyst was exposed to methane but there was no radioactivity found in the gas phase which meant that there was no exchange between methane and surface tritium. However, if hydrogen was admixed to methane in such a quantity that the pressure of the two gases was equivalent, radioactivity appeared first in hydrogen and, with a little delay, in methane. For instance, by introducing a mixture of 50 Hg mm hydrogen and 48 Hg mm methane at 230 °C we observed exchange only between gas hydrogen and surface tritium up to 50 minutes. After raising the temperature up to 270 °C, radioactivity appeared in methane, too.

The kinetic curve can be described by the equation of KEMBALL

$$\frac{d\varrho}{dt} = K(\varrho - \varrho_\infty) \tag{2}$$

where ϱ is the specific radioactivity of methane at time t, and ϱ_∞ at equilibrium. This shows an apparent first order kinetics and the rate constant is constant only for the course of an exchange reaction with a single mixture of reacting gases. True kinetics was determined by the variation of the initial pressure of both methane and hydrogen P = 15.22–75.60 Hg mm and P = 22.14–50.76 Hgmm, respectively. The exchange reaction was found first order with respect to methane and negative order with respect to hydrogen in accordance with the literature. The kinetic equation for methane tritium exchange therefore is:

$$w = k \frac{P_{CH_4}}{P_{HT}} \tag{3}$$

The energy of activation determined by the initial rate method is 34 kcal/mole (Fig. 5), which is 10 kcal more than the previous value found by KEMBALL for the CH_3D formation on Ni film.

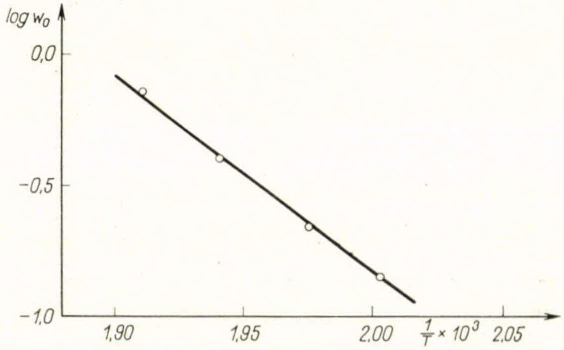

Fig. 5. The logarithm of initial rate of CH_3T formation versus 1/T

Discussion

The main advantage of the use of a tracer amount of tritium in hydrogen for the exchange reaction is the elimination of multiple exchange, *i.e.* it is possible to investigate the behaviour of only one of the hydrogen atoms in the hydrocarbon molecule. The probability of entering more than one tritium atom the hydrocarbon molecule is less than 10^{-5}—10^{-6} depending upon the ratio of tritium to hydrogen. In case of carrier-free deuterium the CH_3D product is not the final one, even according to the multiple exchange mechanism.

Two important points arise from the experimental results.

1. To detect isotopic exchange, H—T and C—H bonds should be broken. The bond strength values (neglecting the isotope effect in case of H—T) are 104 and 101 kcal/mole, respectively. On the surface of Ni, however, these values become much smaller:

$$(Q_{HH})_{Ni} = - Q_{HH} + 2Q_{HNi}$$

and

$$(Q_{CH})_{Ni} = - Q_{CH} + Q_{HNi} + Q_{CNi}$$

Their difference

$$(Q_{HH})_{Ni} - (Q_{CH})_{Ni} = - Q_{HH} + Q_{CH} + Q_{HNi} - Q_{CNi} = Q_{HNi} - Q_{CNi} - 3\,\text{kcal.}$$

Substituting the values for $Q_{HNi} = 55$ kcal [10] and $Q_{CNi} = 17.5$ kcal [11]

$$(Q_{HH})_{Ni} = (Q_{CH})_{Ni} + 34.5 \text{ kcal}$$

It can be seen that in the case of dissociation of H—H on nickel less energy is required than in the case of a C—H bond. Therefore it is conceivable that the H—T bond can be broken much easier and the isotope exchange reaction needs threshold temperature above which methane is adsorbed dissociatively on the catalyst surface and the CH_3 radical formed has a chance to pick up tritium atom from the surface, and after desorption appears in the gas phase as a CH_3T molecule.

The difference in bond strength values on the Ni surface is partly responsible for the experimental fact that by introducing a mixture of H_2 and CH_4 to the catalyst having been exposed by tritium, the exchange starts between hydrogen and surface tritium at lower temperature and at higher temperature at which also the dissociative adsorption of methane can become energetically possible, the tritium starts entering the methane.

2. It is rather difficult to explain the lack of radioactivity in methane when it was introduced alone onto the Ni catalyst previously exposed to tritium. It seems to be rather likely that tritium remained on the surface suffers immobile adsorption and is held rather firmly on the centres having the highest surface energy. They can be only approached by hydrogen from the gas phase resulting in isotope exchange. This is in agreement with results obtained by other authors [12, 13] on Pt, Pd and Ni. In presence of both gases in the gas phase, tritium may be transferred first into the gaseous hydrogen and after re-adsorption it appears in methane. Nevertheless, the heterogeneity of the Ni catalyst shown in one of our previous work [12] may influence this results. Moreover, we need some more information on the methane adsorption on Ni catalyst.

As far as the energy of activation is concerned, our value is 10 kcal/mole higher than KEMBALL's one for CH_3D formation. This difference might probably be explained by the fact that CH_3D is not the sole product (if the exchange is controlled by stepwise mechanism, CH_3D is an intermediate product) and on the other hand this excess energy of activation is due to kinetic isotope effect with regard to the difference in the reactivity of deuterium and tritium atoms in the surface layer.

The authors are grateful to Dr. T. SZARVAS for valuable discussion and indebted to K. KOLLÁR for technical assistance.

SUMMARY

Experiments have been carried out on the isotope exchange between CH_4 and HT on Ni catalyst. The kinetics of the reaction was studied and the activation energy value was calculated.

It is stated, that the exchange between H—T and H_2 goes easier and quicker than that between CH_4 and HT. This fact is in accordance with the results of thermodynamical calculations and can be explained with the more rapid adsorption of hydrogen.

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КОЛЕБАТЕЛЬНЫЕ СПЕКТРЫ И ПОВОРОТНАЯ ИЗОМЕРИЯ НЕКОТОРЫХ ЭТИЛХЛОРСИЛАНОВ

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Настоящая работа посвящена изучению колебательных спектров и поворотной изомерии некоторых этил-хлор замещенных Si. Эти соединения имеют большую практическую ценность и поэтому в последнее время уделяется значительное внимание изучению их физикохимических свойств и строения молекул. Однако данных по колебательным спектрам этих соединений крайне недотаточно, причем расчет частот и форм нормальных колебаний рассматривсемых молекул не проводился: а вопросы поворотной изомерии, возможаой у многих этильных производных Si при заторможенном внутреннем нращении вокруг связи Si — C количественно никем не рассматривалисьв

Получение. этих данных необходимо прежде всего для статистических расчетов термо инамических функций и химических равновесий газовых реакций. Работа была поставлена в лаборатории молекулярной спектроскопии Химического факультета МГУ.

Исследование представляет также и теоретический интерес.

Для изучения нами были выбраны три простейшие молекулы: $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$, $C_2H_5SiH_2Cl$. В случае $C_2H_5SiCl_3$ поворотная изомерия невозможна. В случае $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ принципиально возможно существование поворотных изомеров (гош- и транс-, см. рис. 1) при заторможенном внутреннем вращении вокруг связи Si—C.

Дляэтих соединений в литературе имелись только неполные данные по ИК спект ру $C_2H_5SiCl_3$[1], и спектрам КР жидких $C_2H_5SiCl_3$ [2—4] и $C_2H_5SiHCl_2$ [3—5]. Поэтому перед нами встала задача самого детального изучения этих соединений как экспериментальными, так и расчетными методами колебательной спектроскопии.

Были получены ИК-спектры и спектры КР всех исследуемых молекул в жидком и твердом агрегатных состояниях и при различных температурах, а также ИК-спектры паров этих веществ [6—8]. Наши экспериментальные результаты для жидких и твердых этилхлорсиланов приведены в таблицах 1—3. Из таблиц видно, что при затвердевании веществ значительно изменяются спектры молекул $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ (в столб. «тв» прочеркнуты исчезающие полосы). Известно [9, 10], что изменения в спектрах в этом случае могут происходить и по другим причинам, а именно за счет эффектов кристалличности и межмолекулярных взаимодействий (в литературе есть указания о наличии ассоциаций в хлорсиланах через Si...Cl).

Оценить величину этих эффектов помогает исследование колебательного спектра $C_2H_5SiCl_3$, где принципиально невозможно существование поворотных изомеров и все изменения в спектрах могут быть связаны только

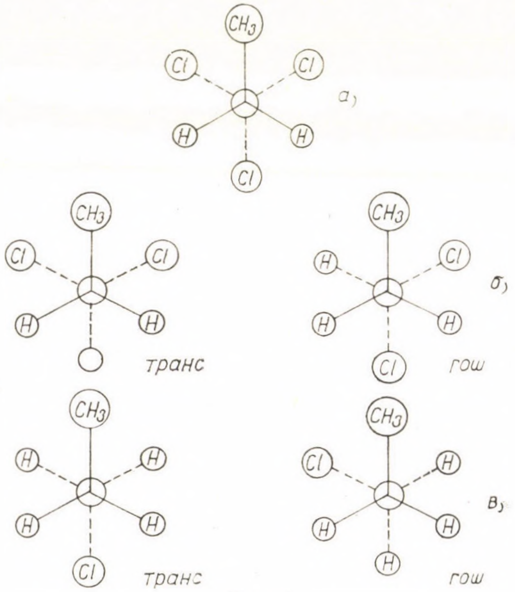

Рис. 1

с указанными выше эффектами. Исследование колебательных спектров жидкого и твердого $C_2H_5SiCl_3$ показало, что все изменения (незначительный сдвиг, сужение и расщепление полос) в спектре твердого соединения могут быть объяснены статическим эффектом поля кристалла и эффектом резонансного взаимодействия соседних молекул в элементарной ячейке кристалла (причем величина этих эффектов мала).

Сравнение колебательных спектров жидкого и газообразного $C_2H_5SiCl_3$ показало [6], что это соединение не имеет сильных межмолекулярных взаимодействий.

Исследование колебательных спектров жидкого и газообразного $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ показало [7, 8], что число экспериментально наблюдаемых частот (достаточно интенсивных полос) существенно превосходит число теоретически ожидаемых для одной равновесной ядерной конфигурации. На основании только этого факта можно сделать предположение, что в жидкости и газе $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ существует в виде двух поворот-

Таблица 1

Колебательный спектр этилдихлорсилана

Обозначение	Тип симметрии	Отнесение (условно)	Рассчитанные частоты ν *см*$^{-1}$	Экспериментальные данные, ν *см*$^{-1}$			
				ИК		КР	
				ж.	тв.	ж.	тв.
ν_1	A''	τ (SiCl$_3$)	85	—	—	—	—
ν_2	A''	ϱ (SiCl$_3$) (r)	143	—	—	131	122 (5)
ν_3	A'	ϱ(SiCl$_3$) (w)	151	—	—	154	154 (5)
ν_4	A'	δ (SiCl)$_3$	188	—	—	183	183 (8)
ν_5	A''	τ (CH$_3$)	202	—	—}	—	—
ν_6	A'	δ (SiCl$_3$)	230	—	—}	225	225 (10)
ν_7	A''	δ (SiCl$_3$)	242	—	—	230	230 (0)
ν_8	A'	δ (CCSi)	304	—	—	327	325 (10 p)
ν_9	A'	ν (SiCl)	454	449 с.	449	448	449 (49 p)
		$\nu_4 + \nu_8$		488 о. сл.	488	—	—
		$\nu_6 + \nu_8$		528 о. сл.	528	—	—
ν_{10}	A''	ν (SiCl)	567	559 о. с.	560	556	561 (2)
ν_{11}	A'	ν (SiCl)	590	589 о. с.	589	600	589 (2)
		$\nu_4 + \nu_9$		617 с.	616	—	—
		$\nu_6 + \nu_9$		665 о. сл.	665	—	—
ν_{12}	A''	ϱ (CH$_2$) (r)	705	703 о. с.	703	—	—
ν_{13}	A'	ν (SiC)	731	722 с.	723	724	721 (2 p)
		$\nu_7 + \nu_{10}$		775 о. сл.	780	—	—
		$\nu_6 + \nu_{11}$		790 о. сл.	794	—	—
		$\nu_2 + \nu_{12}$		804 сл.	809	—	—
		$\nu_2 + \nu_{13}$		818 сл.	823	—	—
ν_{14}	A''	ϱ (CH$_3$) (r)	965	965 ср.	961	968	—
ν_{15}	A'	ϱ (CH$_3$) (w)	989	975 сл.	975	980	980 (2)
ν_{16}	A'	ν (C — C)	1032	1010 с.	{1009		
					{1018	1016	1016 (3)
ν_{17}	A''	ϱ (CH$_2$) (t)	1234	1226 ср.	1225	1225	1225 (1)
ν_{18}	A'	ϱ (CH$_2$) (w)	1238	1244 ср.	1244	1245	1247 (2 p)
ν_{19}	A'	δ (CH$_3$)	1382	1384 ср.	1381	1385	1392 (1)
ν_{20}	A'	δ (CH$_2$)	1407	1418 сл.	1418	1422	1420 (1)
ν_{21}	A'	δ (CH$_3$)	1466}	1463 с.	1451	1457	1464 (3)
ν_{22}	A''	δ (CH$_3$)	1476}		1475	1470	
		2 ν_{19}		—	—	2750	2750 (1)
		$\nu_{19} + \nu_{21}$		2836 сл.	2835	2840	2840 (1)
		2 ν_{21}		2885 ср.	2885	2885	2886 (7 p)
ν_{23}	A'	ν (CH$_3$)	2900	2898 сл.	2898	2897	2897 (12 p)
		2 ν_{22}		2914 о. сл.	2914	2925	2932 (4)
ν_{24}	A'	ν (CH$_2$)	2944	2941 ср.	2941	2940	2941 (10 p)
ν_{25}	A''	ν (CH$_3$)	2973}				
ν_{26}	A'	ν (CH$_3$)	2976}	2973 с.	2973	2973	2973 (6)
ν_{27}	A''	ν (CH$_2$)	2992	—	—	2985	2985 (1)

Примечание: Сокращения и условные обозначения в табл. 1—3: ИК — инфракрасный спектр; КР — спектр комбинационного рассеяния; ж. — жидкость; тв. — твердое; τ — крутильные колебания; δ — внутренние деформационные колебания (ножничные); ϱ — внешние деформационные колебания (r — маятниковое, w — веерное или зонтиковое; t — крутильно-деформационное); ν — валентные колебания; о. с. — очень сильная; с — сильная; ср. — средняя; сл. — слабая; о. сл. — очень слабая; р — поляризованная линия КР., число в скобках указывает интенсивность линий КР в десятибальной шкале.

Таблица 2

Колебательный спектр этилдихлорсилана

Обозначение		Тип симметрии для *транс*-формы	Отнесение (условно)	Рассчитанные частоты, ν *см*$^{-1}$		Экспериментальные данные, ν *см*$^{-1}$			
гош-форма	*транс*-форма					ИК		КР	
				гош-форма	*транс*-форма	ж. (*транс*- + *гош*)	тв. (*транс*)	тв. (*транс*)	ж. (*транс*- + *гош*)
ν_1		A″	τ ($SiHCl_2$)	114	75			?	?
			?			—	—	146	146 (1)
	ν_2	A′	ϱ ($SiCl_2$) (w)		170	—	—	167	?
ν_2				169		—	—		177 (7)
ν_3		A′	δ ($SiCl_2$)	189	190	—	—	193	187 (4)
ν_4		A″	τ (CH_3)	200	192	—	—	227	227 (0)
ν_5		A″	ϱ ($SiCl_2$) (r)	264	263	—	—	265	271 (1)
ν_6				282		—	—	—	293 (5 р)
	ν_6	A′	δ (CCSi)		352	—	—	372	372 (1)
	ν_7	A′	ν (SiCl)		486	490 с.	485	478	486 (22р)
ν_7				499		плечо	—	—	плечо
	ν_8	A″	ν (SiCl)		549	543 с.	538	543	550 (2)
			$2\nu_5$				плечо	—	—
ν_8			ν (SiCl)	558		556 с.	—	—	559 (2)
			$\nu_5 + \nu_6$			613 ср.	613	—	—
ν_9		A″	ϱ (CH_2) (r)	687	682	659 ср.	660	668	660 (6)
	ν_{10}	A′	ν (SiC)		698	680 сл.	679	688	680 (0)
ν_{10}				704		708 ср.	—	—	708 (4 р)
ν_{11}		A″	δ (HSiCl)	807	811	—	—	799	799 (3)
ν_{12}		A′	δ (HSiC)	813	817	806 о. с.	806	807	810 (3)
ν_{13}		A″	ϱ (CH_3) (r)	968	966	966 ср.	966	—	—
ν_{14}		A′	ϱ (CH_3) (w)	991	985	975 сл.	975	978	978 (3)
ν_{15}			ν (CC)	1041		1014 сл.	—	—	1012 (2)
	ν_{15}	A′			1041	1020 ср.	1020	1019	1019 (1)
ν_{16}		A″	ϱ (CH_2) (t)	1232	1230	1227 сл.	1232	1232	1227 (0)
ν_{17}		A′	ϱ (CH_2) (w)	1244	1239	1241 сл.	1246	1246	1240 (2 р)
ν_{18}		A′	δ (CH_3)	1385	1382	1382 сл.	1382	—	—
ν_{19}		A′	δ (CH_2)	1412	1410	1406 сл.	1406	1407	1407 (2)
ν_{20}		A′	δ (CH_3)	1467	1464	1462 ср.	1462	1462	1462 (3)
ν_{21}		A″	δ (CH_3)	1486	1483				
ν_{22}		A′	ν (SiH)	2203	2204	2207 с.	2216	2208	2208 (19 р)
			$\nu_{18} + \nu_{20}$			2836 сл.	2836	2832	2832 (0)
			$2\nu_{20}$			2880 ср.	2880	2883	2883 (13 р)
ν_{23}		A′	ν (CH_3)	—	2890	2897 сл.	2897	2900	2900 (12 р)
			$2\nu_{21}$			2916 сл.	2916	2919	2919 (5)
ν_{24}		A′	ν (CH_2)	—	2942	2936 сл.	2936	2940	2940 (10 р)
ν_{25}		A″	ν (CH_3)	—	2973	2967 ср.	2967	2968	2968 (6)
ν_{26}		A′	ν (CH_3)	—	2976				
ν_{27}		A″	ν (CH_2)	—	2990			2983	2983 (0)

Таблица 3

Колебательный спектр этилдихлорсилана

Обозначение		Тип симметрии для *транс*-формы	Отнесение (условно)	Расститанные частоты, ν см$^{-1}$		Экспериментальные данные, ν см$^{-1}$			
						ИК		КР	
гош-форма	*транс*-форма			*гош*-форма	*транс*-форма	ж. (*транс* + *гош*)	тв. (*гош*)	тв. (*гош*)	ж. (*транс* + *гош*)
ν_1		A′′	τ (SiH$_2$Cl)	103	114	—	—	?	?
			?			—	—	152	152 (0)
ν_2			δ (ClSiC) {	159		—	—	164	161 (3)
	ν_2	A′			197	—	—	—	187 (0)
ν_3		A″	τ (CH$_3$)	214	200	—	—	222	222 (0)
	ν_4	A′	δ (CCSi) {		258	—	—	—	245 (0)
ν_4				300		—	—	292	285 (4 p)
			2 ν_2						295 (0)
ν_5			ν (SiCl) {	496		плечо	497	496	плечо } (12p)
	ν_5	A′			512	509 с.		—	509 }
ν_6	ν_6	A″	ϱ (SiH$_2$) (r) {		552	529 ср.	—	—	529 (1)
ν_7				552		565 ср.	563	567	563 (3)
ν_8		A′′	ϱ (CH$_2$) (r)	684	680	653 ср.	653	655	657 (5)
	ν_8	A′	ν (SiC) {	681		682 } с.	687	686	682 } (6 p)
ν_9					683	693 }	—	—	693 }
	ν_9	A″	ϱ (SiH$_2$) (t) {	742		744 с.	746	746	745 (4)
					744	770 ср.	—	—	770 (0)
ν_{10}		A′	ϱ (SiH$_2$) (w)	883	879	854 о. с.	855	852	856 (3)
ν_{11}		A′	δ (SiH$_2$)	930	929	950 о. с.	950	944	949 (6)
ν_{12}		A″	ϱ (CH$_3$) (r)	973	965	—	972	968	—
ν_{13}		A′	ϱ (CH$_3$) (w)	992	991	978 с.	980	982	979 (3)
	ν_{14}	A′	ν (CC) {		1037	1012 ср.	—	—	1012 (2)
ν_{14}				1039		1025 ср.	1026	1030	1026 (1)
			$\nu_5 + \nu_7$			1140 о.сл	1145	—	—
			$\nu_5 + \nu_8$			1185 о.сл	1186	—	—
ν_{15}		A′′	ϱ (CH$_2$) (t)	1225	1224	1236 ср.	1231	1232	1226 (1)
ν_{16}		A′	ϱ (CH$_2$) (w)	1247	1246	—	1245	1247	1240 (3 p)
			$\nu_4 + \nu_{14}$			1302 о.сл	1302	—	—
ν_{17}		A′	δ (CH$_3$)	1387	1381	1384 сл.	1384	1385	1382 (1)
ν_{18}		A′	δ (CH$_2$)	1414	1413	1412 ср.	1411	1414	1411 (2)
ν_{19}		A′	δ (CH$_3$)	1471	1464 }	1465 ср.	1465	1467	1466 (4)
ν_{20}		A′′	δ (CH$_3$)	1490	1485 }				
ν_{21}		A′	ν (SiH)	2180	2177 }				
ν_{22}		A′′	ν (SiH)	2180	2182 }	2174 о.с.	2185	2176	2176 (40 p)
			$\nu_{17} + \nu_{19}$	—	—	2835 сл.	2840	2835	2835 (0)
			2 ν_{19}	—	—	2879 с.	2979	2877	2879 (13 p)
ν_{23}		A′	ν (CH$_3$)	—	2901	2891 сл.	2891	2893	2890 (11 p)
			2 ν_{20}	—		2912 сл.	1914	2922	2915 (8)
ν_{24}		A′	ν (CH$_2$)	—	2934	2935 сл.	2934	2934	2938 (10 p)
ν_{25}		A′′	ν (CH$_3$)	—	2971 }	2961 с.	2962	2966	2965 (8)
ν_{26}		A′	ν (CH$_3$)	—	2976 }				
ν_{27}		A″	ν (CH$_2$)	—	2984 }				

ноизомерных форм (гош- и транс-), которые принципиально возможны в этих двух случаях. Сравнение колебательных спектров этих молекул в жидком и твердом состояниях подтверждает высказанное выше предположение. При затвердевании $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ происходит значительное упрощение их колебательных спектров, что можно объяснить изменением изомерного состава этих соединений. Число экспериментально наблюдаемых частот в твердой фазе соответствует одной равновесной ядерной конфигурации молекул этилди- и этилмонохлорсиланов.

Таким образом, из анализа экспериментальных данных видно, что колебательные спектры жидких и газообразных $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ представляют наложение спектров гош- и транс-поворотно-изомерных форм, а колебательные спектры твердой фазы соответствуют одной поворотно-изомерной форме.

Но только из результатов эксперимента еще не удается установить соответствие наблюдаемых частот тому или иному поворотному изомеру в различных агрегатных состояниях. Для решения этого вопроса использованы результаты расчета частот и форм нормальных колебаний для гош- и транс-равновесных ядерных конфигураций $C_2H_5SiHCl_2$ [11] и $C_2H_5SiH_2Cl$ [8] и для одной возможной «шахматной» конфигурации $C_2H_5SiCl_3$ [6].

Расчет колебаний молекул был проведен по методике Ельяшевича, Степанова [12] и Маянца [13] с учетом крутильных координат. Силовые коэффициенты были взяты из работ [12, 14—16] по расчету колебаний следующих молекул: CH_3SiCl_3; $(CH_3)_3SiH$; $(CH_3)_2SiCl_2$; $(CH_3)_2SiH_2$; $(CH_3)_3SiCl$; C_2H_6; C_3H_8; $C_2H_4Cl_2$. Вековые уравнения решены в предположении, что с изменением равновесной ядерной конфигурации силовое поле сохраняется. Кроме того, при решении колебательной задачи для гош-формы проводилось отделение высоких частот валентных колебаний CH от остальных частот по методу Вильсона[17]. Эта операция абсолютно никак не сказывается на низкочастотной области спектра, по которой делаются все выводы относительно равновесных ядерных конфигураций молекул. Вековые уравнения решены на электронновычислительной машине «Стрела» по программе А. М. Богомолова.

Результаты вычисления частот нормальных колебаний молекул для предполагаемых ядерных конфигураций представлены в табл. 1—3. Из сравнения экспериментальных и расчетных данных, приведенных в табл. 2—3, видно, что «вымораживающимися» являются те частоты, которые относятся к гош-форме в случае $C_2H_5SiHCl_2$ и к транс-форме в случае $C_2H_5SiH_2Cl$.

В твердом состоянии первое соединение существует в виде транс-, второе (при медленной кристаллизации) — в виде гошповоротно-изомерных форм, в противном случае в твердом состоянии сохраняются гош- и транс-формы молекулы $C_2H_5SiH_2Cl$.

Проведена полная интерпретация колебательных спектров исследуемых молекул [6, 8, 11] на основании рассчитанных форм нормальных колебаний, измеренных степеней деполяризации линий КР, рассмотрения контуров полос ИК-поглощения газов, а также анализа литературных данных по исследованию спектров родственных соединений. Отнесение частот представлено в табл. 1—3.

Спектроскопически удается определить не только равновесные ядерные конфигурации исследуемых молекул, но и установить относительную устойчивость поворотных изомеров, т. е. оценить ΔE — разность их энергий, а также концентрационные соотношения.

Интенсивность полос колебательного спектра пропорциональна концентрации поворотных изомеров. Изучая перераспределение с температурой интенсивности полос, принадлежащих различным изомерам, можно определить ΔE по формуле:

$$\left(\frac{I\textit{гош}}{I\textit{тр}}\right)_{T_1} : \left(\frac{I\textit{гош}}{I\textit{тр}}\right)_{T_2} = \exp\frac{\Delta E}{R}\left(\frac{1}{T_2} - \left(\frac{1}{T_1}\right)\right.$$

Формула получена интегрированием уравнения изохоры реакции поворотной изомеризации в предположении $\Delta E = \mathrm{const}$ в данном температурном интервале, и $\frac{I\textit{гош}}{I\textit{тр}}$ не зависит от T.

В ряде работ было показано [18—20], что при небольших температурных интервалах измерения допустимо считать $\Delta E = \mathrm{const}$ и $\frac{I\textit{гош}}{I\textit{тр}}$ можно считать независимым от T, если для измерения выбрать полосы близких по форме колебаний. Достоверность получаемых значений ΔE может быть проверена путем сопоставления результатов определения ΔE несколькими независимыми методами (в нашем случае методом ИК-спектров, спектров КР и по разным парам полос одного и того же спектра, но относящимся к разным по форме колебаниям).

Для молекул $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ в интервале температур — 100—20° С определены разности энергий поворотных изомеров [21]. В таблице 4 показаны полосы, по которым проводилось исследование, дано их отнесение, указан метод определения ΔE (ИК-спектров и спектров КР), приведены результаты определения ΔE различными методами и среднее значение всех независимых определений. Полученные выше результаты позволяют сделать вывод о большей устойчивости транс-изомера в случае $C_2H_5SiHCl_2$, и гош-изомера в случае $C_2H_5SiH_2Cl$. Результаты определения ΔE для жидкого $C_2H_5SiH_2Cl$ согласуются с аналогичными данными [22] для $C_2H_5CH_2Cl$: в обоих случаях $\Delta E_{г-тр} \approx -0{,}3\,\frac{\text{ккал}}{\text{моль}}$

Таблица 4

Разности энергий и концентрационные соотношения поворотных

Соединение	Метод определения			
	ИК-спектры			
	ν, см$^{-1}$		условное отнесение	ΔE, $\frac{\text{кал}}{\text{моль}}$ (г — тр)
	гош	транс		
$C_2H_5SiHCl_2$	708	680	ν (SiC)	370 ± 70
$C_2H_5SiH_2Cl$	744 1026	770 1012	ϱ (SiH^2)t ν (CC)	—350 ± 80 —300 ± 80

Найденные значения ΔE использованы для определения концентрационных соотношений поворотных изомеров жидких $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ по формуле:

$$\frac{N_1}{N_2} \frac{\sigma_1}{\sigma_2} \frac{{}_iQ_{1i}}{{}_jQ_{2j}} \exp\left(\frac{-\Delta E}{RT}\right)$$

$\frac{\sigma_1}{\sigma_2} = 2$ — отношение статистических весов поворотных изомеров;

${}_iQ_i$ — произведение статистических сумм изомеров.

Мольные доли гош-изомера при 250° К приведены в табл. 4.

Кроме разности энергий поворотных изомеров, важной характеристикой заторможенного внутреннего вращения является высота потенциального барьера (V_0). Нам не удалось экспериментально найти крутильные частоты $\geqslant$SiCl групп, а следовательно, экспериментально оценить V_0. Величины барьеров заторможенного внутреннего вращения относительно связи Si — C нами определены для всех исследованных молекул по методу Маняско [23], которые оказалисьр авными $V_{0г-тр} = 3{,}05$; 2,66; 1,97 соответственно для $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$.

Метод Маняско не имеет строгого физического обоснования, тем не менее для простейших молекул с тетраэдрической системой валентных связей с его помощью получаются значения V_0, близкие к определенным экспериментально и в нашем случае его применение вполне допустимо. Метод Маняско в случае алкилхлорсиланов — единственно возможный метод определения величины барьера, т. к. его применение в противоположность другим эмпирическим методам не требует знания высот барьеров простейших хлорсиланов, которые в литературе отсутствуют.

изомеров этилдихлорсилана и этилмонохлорсилана

Метод определения				$\overline{\Delta E}$, кал/моль (среднее)	Мольная доля гош-изомера (250° К)
спектры КР					
ν, см$^{-1}$		условное отнесение	$\Delta E, \frac{\text{кал}}{\text{моль}}$ (г — тр)		
гош	транс				
708	680	ν (SiC)	350 ± 70	400	~ 0,47
293	372	δ (CCSi)	490 ± 80		
565	529	ϱ $(SiH_2)r$	−180 ± 120	−280	~ 0,78

ВЫВОДЫ

1. Изучены ИК-спектры в области 400—3000 см$^{-1}$ и спектры КР $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ в различных агрегатных состояниях и при различных температурах.

2. Проведен полный расчет частот, и форм нормальных колебаний молекул исследуемых соединений для всех принципиально возможных равновесных ядерных конфигураций: одной «шахматной» конфигурации $C_2H_5SiCl_3$, гош- и транс-конфигураций $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$. Проведена полная интерпретация колебательных спектров исследуемых этилхлорсиланов.

3. Сопоставлением экспериментальных данных по «вымораживанию» частот с результатами расчета показано, что в кристаллическом состоянии в случае $C_2H_5SiHCl_2$ сохраняется транс-, а в случае $C_2H_5SiH_2Cl$ (при очень медленной кристаллизацией) гош-равновесные ядерные конфигурации молекул. В жидкости и газе имеется подвижное равновесие гош- и транс-поворотно-изомерных форм этих молекул.

4. Исследованием температурной зависимости относительной интенсивности полос, принадлежащих различным изомерам, определены разности энергий гош- и транс-поворотных изомеров $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ в жидкой фазе, которые оказались равными 0,4 ккал/моль — для первого (транс-форма более устойчива) и — 0,3 ккал/моль для второго (гош-форма более устойчива). На основании этих результатов оценены концентрационные соотношения поворотных изомеров: при 250° К мольные доли гош-формы ди- и монохлорпроизводных равны соответственно 0,47 и 0,78.

5. Эмпирическим методом Маняско оценены потенциальные барьеры внутреннего вращения молекул $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$ и $C_2H_5SiH_2Cl$ относительно связи Si — C.

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Infrared spectra and rotamers of a few ethylchlorosilanes

YU. A. PENTIN and C. E. RUDAKOVA

Summary. 1. The infrared and Raman spectra of $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$ and $C_2H_5SiH_2Cl$ have been studied in the range from 400 to 3000 cm^{-1} in different states and at different temperatures.

2. For all theoretically possible equilibrium configurations the total frequencies and the normal coordinates of the investigated compounds have been calculated, thus, for the "checkerboard configuration" of $C_2H_5SiCl_3$, and for the *gauche* and *trans* rotamers of $C_2H_5SiHCl_2$ and $C_2H_5SiH_2Cl$. Complete interpretations of the vibrational spectra of the investigated ethylchlorosilanes are given.

3. It is shown by comparison of the experimental frequency data, obtained by "freezing out", with the calculated results that in the crystalline state the *trans* equilibrium configuration is preserved in the case of $C_2H_5SiHCl_2$, and (under very slow crystallization) the *gauche* equilibrium configuration in the case of $C_2H_5SiH_2Cl$. In liquid and gaseous state, the *gauche-trans* or *trans-gauche* forms of these molecules are present in dynamic equilibrium.

4. By the investigation of the temperature dependence of the intensities of the bands assigned to the various isomers, the energy differences in the liquid phase of the *gauche* and *trans* isomers of $C_2H_5SiHCl_2$ and $C_2H_5SiH_2Cl$ have been determined. These are as follows: 0.4 kcal/mole for the first compound (the *trans* form is more stable), and —0.3 kcal/mole for the second compound (the *gauche* form is more stable). On the basis of these results, the concentration ratio of the isomers has been determined: at 250°K, the molar fractions of the *gauche* forms of the di- and monochloro derivatives are 0.47 and 0.78, respectively.

5. The potential barriers of the internal rotation of the $C_2H_5SiCl_3$, $C_2H_5SiHCl_2$ and $C_2H_5SiH_2Cl$ molecules about the Si—C linkage have been evaluated by the empirical method of Magnascko.

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SOME TOPOLOGICAL FEATURES OF COVALENTLY BONDED MOLECULES

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Introduction

Modern structural research often investigates molecules considering them as spatial formations. Problems of this nature arise in the course of calculations of molecular vibration, in the theory of electronic spectra, *etc.*

In the course of these investigations the molecule is considered as a set of points (atoms) and lines (valence lines) ordered in a some way.

As geometric formations the molecules may be examined from two points of view:

a) Certain fixed quantities (their lengths) are assigned to the lines of the molecules as geometric formations. The structure is fixed by giving the angles between these lines. There are points, lines and planes in the space which are at equal distance of at least two atoms of the structure fixed in this way. The atoms at equal distance from such a point, line or plane are called equivalent atoms. If these lines, points and planes are such that all the atoms of the molecule belong to an equivalent atomic set or are placed within the latter, these geometrical elements are called the symmetry elements of the molecule. The operators $\hat{\mathbf{R}}$, interpreted for a molecule, which transpose the atoms of an atomic set pertaining to a symmetry element into each other's place are called symmetry operators. Symmetry operators that interchange neighbouring atoms transform the lines connecting them into equivalent lines.

The symmetry operators from a group, thus investigations of this type are discussed by the group theory. The symmetry conditions of molecules has been studied very thoroughly and since a long time [1, 2, 3, 4].

b) Far less work has been done on the bonding conditions between the atoms in the molecule. PÓLYA [5] has studied the number of possible isomers. In such cases the molecule is not considered as a rigid one. The bonding conditions may be studied by another branch of algebra, namely by the graph theory.

The molecule as a graph

A graph ($\mathcal{G}$) is a set X of points if at the same time there is interpreted an operator $\hat{\mathbf{\Gamma}}$ transforming the points into neighbouring points:

$$\mathcal{G} = (\mathcal{X}, \hat{\mathbf{\Gamma}}) \tag{1}$$

To have operator $\hat{\mathbf{\Gamma}}$ defined in this way is equivalent to proposing a set $\mathcal{U}$ of lines which connect the neighbouring vertices. The points $x \in X$ are called the vertices, the lines $u \in \mathcal{U}$ are the arcs of the graph. Obviously the molecules may be considered as graphs, too, if their atoms are the vertices and their valence lines the arcs.

A graph may be oriented if its arcs have a direction. The adjusting coefficient (ε) of the arc and vertex may be introduced. For the vertex x_i wherefrom the arc u_{ij} starts, is

$$\varepsilon_{ij} = (x_i, u_{ij}) = -1 \tag{2}$$

and for the vertex the same arc ends in:

$$\varepsilon_{ji} = (x_j, u_{ij}) = +1 \tag{3}$$

Thus the formal interchange of the indices of the adjusting coefficient results in a change of the sign.

The graph is imagined as a formation constructed of the edges of some "polyhedron". The regions of such "polyhedrons" may have different dimensions. As the faces of the polyhedron are not necessarily planes, for unique assignment the graph or its regions have to be projected on a plane.

A geometrical formation is called in-plane, when it is homeomorphous with a formation which can be unfolded into a single plane without intersecting itself [6]. If this condition is not fulfilled the formation is in-space.

Let $\mathcal{P}$ be the polyhedron obtained from the graph of the molecule by projection of its in-plane two dimensional regions on planar formations homeomorphous with it, without a self-intersection of the three dimensional regions. In this case there is a reversible unique assignment between the polyhedron $\mathcal{P}$ of the molecule and its graph $\mathcal{G}$:

$$\mathcal{P} \cong \mathcal{G} \tag{4}$$

The index of the vertex of the graph, φ, is the number indicating the number arcs to which this vertex is linked (the number of atoms to which this atom is bonded):

$$\varphi_i = \sum |(x_i, u_{ij})| = \sum_j |\varepsilon_{ij}| \tag{5}$$

Vertices of the graph of the molecule having index $\varphi_i \geqq 2$ and the operator $(\hat{\mathbf{\Gamma}}_V)$ transforming these into the neighbouring vertices determine a subgraph of graph $\mathcal{G}$, the skeleton $\mathcal{V}$ of the molecule [8]

$$\mathcal{V} \subseteq \mathcal{G} \qquad \mathcal{V} = (x_i\,[\varphi_i \geqq 2], \hat{\mathbf{\Gamma}}_V) \tag{6}$$

There is again a reversible unique assignment, between the skeleton and the polyhedron, $\mathcal{P}_V$, assigned to it:

$$\mathcal{P}_V \cong \mathcal{V} \tag{7}$$

If a polyhedron is resolved into its elements then zero, one, two or three dimensional formations are obtained (so-called cells) [6], which are designated as peaks, edges, planes and polyhedrons, respectively. The resolution of the formation in this way is a so-called cell-resolution. If the dimension of the largest cell obtained by the cell-resolution of the polyhedron $\mathcal{P}_V$ is

- zero, then the molecule has a central structure *(e.g.* methane);
- one, then the molecule is a chain *(e.g. n*-butane);
- two, then the molecule has an in-plane cyclic structure *(e.g.* cyclohexane)
- tree, then the molecule has an in-space cyclic structure *(e.g.* hexamethylene-tetramine)

A connected graph is called a tree [6] if any two vertices of it may be connected by a single line

$$\mathcal{U}_{1n} = (x_1\, u_{12}\, x_2 \ldots x_{n-1}\, u_{n-1,n}\, x_n)$$

The subgraph, of which no tree can be constructed by addition of any other arc of the graph, is the maximum tree of the graph. It holds for molecules having a central structure

$$\varnothing = \mathcal{T}_V = \mathcal{V} \subset \mathcal{T} \tag{8}$$

where $\varnothing$ stands for the empty set.

For chain molecules

$$\mathcal{T}_V = \mathcal{V} \subset \mathcal{T} \tag{9}$$

For cyclic molecules

$$\mathcal{T}_V = \mathcal{V} \cap \mathcal{T} \tag{10}$$

Let us introduce now the concept of cell boundary. The boundary of the zero dimensional cell (peak) is zero. The boundary of the one dimensional cell (for boundary formation the symbol $\varDelta$ is used):

$$\varDelta u_{ij} = \varepsilon_{ij}\, x_i + \varepsilon_{ji}\, x_j = x_j - x_i \tag{11}$$

The boundary of the two dimensional cell may be obtained in the following way: on the face g_k a circulatory direction is chosen (Fig. 1). The adjustment coefficient μ_{ij}^{k} of the face g_k to the arc u_{ij} is $+1$ if the direction of circulation agrees with the direction of the edge, and -1 if the two directions are opposite:

$$\Delta g_k = \sum_{ij} \mu_{ij}^{k} u_{ij} \tag{12}$$

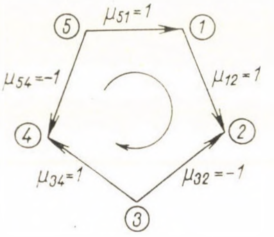

Fig. 1

The boundaries of the polyhedron p_l are obtained by assigning a value of $+1$ to the adjustment coefficient ϱ if from the inside of the polyhedron the direction of circulation is right handed, and the value -1 if this direction is left handed:

$$\Delta p_l = \sum \varrho_k^{l} g_k \tag{13}$$

The cyclic trunk of the molecule $\mathscr{T}$ is a graph correlated to the set of cells obtained by cell division and has a dimension of at least 2:

Fig. 2

$$\mathscr{T} \subseteq \mathscr{V} \qquad (\mathscr{P}_T \subseteq \mathscr{P}_V) \tag{14}$$

$\mathscr{T}$ is a subgraph, and the polyhedron $\mathscr{P}_T$ is not necessarily connected. If $\mathscr{P}_T$ is not connected then at least some of the cycles of the molecule are isolated. If the common section of two faces (g_r and g_s) of the polyhedron $\mathscr{P}_T$ is a path

$$\Delta g_r \cap \Delta g_s = \bigcup_{(ij)} u_{ij} \neq \varnothing \; (g_r, g_s \in \mathscr{P}_T) \tag{15}$$

then the two are condensed. If for the arcs g_r and g_s forming the boundaries of u_{ij}^r and u_{ij}^s the common vertex is given by

$$\bigcup_{(ij)} \bigcup_{(pq)} [\Delta u_{ij}^r \cap \Delta u_{pr}^s]\, x_t \quad (g_r, g_s \in \mathscr{P}_T) \quad (x_t \in \mathscr{T}) \tag{16}$$

then the link between the two rings has a spiro-character.

Interpretation of scalar quantities on the graph

Let us now assign certain functions to the arcs $u_{ij} \cdot f(u)$ should be the function having the value of unity for all arcs, and $g(u)$ the function indicating the number of bonding electrons for each covalent valence line. For σ bonds (with the exception of very long chains) the value of $g(u)$ is an integer, while for π bonds, especially for conjugated π bonds this is normally not the case.

In the graph theory the load of a function on a certain vertex x_i is given by the following expression:

$$|f, x_i| = \sum_j |f(u_{ij})| \,.\, |(x_i, u_{ij})| = \varphi_i \tag{17}$$

Thus Equation (17) is the index of the vertex x_i. For the function

$$|g, x_i| = \sum_j |g(u_{ij})| \,.\, |x_i, u_{ij}| = \gamma_i \tag{18}$$

The quantity γ_i is the overall electron density of the valence lines (arcs) joined to x_i. The half of γ_i is equal to the number of valencies of the atom x_i for σ bonds and isolated π bonds, and to the sum of the number of σ bonds and of half of the delocalized π electron density on the valance lines joined to the atom for conjugated π electron systems.

In a molecule a subset of the skeleton is called a chain (in the chemical sense [8]), if the atoms in the molecule form an unbranched structure in which some atoms are linked to not more than two other atoms of the structure. In the graph theory the simple path corresponds to the chemical conception of a chain. The simple path is a path which leads from one vertex to the other by touching each vertex and each arc only once (with the exception of the first and last ones):

$$\mathscr{U}_{1n} = (x_1\, u_{12}\, x_2 \ldots x_{n-1}\, u_{n-1,\,n}\, x_n); \; [\bigcap_{ij} u_{ij} = \varnothing, \bigcap_{1=2}^{n-1} x_i = \varnothing] \tag{19}$$

If the first and the last vertices are identical, *i.e.* $x_i = x_n$ then we have a circular path corresponding to the chemical conception of a ring. If it holds for two simple paths $\mathbf{U}_{ab}$ and $\mathbf{U}_{cd}$

$$\mathscr{U}_{ab} \cap \mathscr{U}_{cd} = \emptyset \tag{20}$$

then these two are independent of one another.

Structural matrix

With the aid of the absolute values of the individual arc-vertex adjustment coefficients (2) the structure of the molecule may be fixed in matrix form [9]. The rows of this structural matrix $\mathbf{C}$ are arranged according to the arcs, and the columns according to the vertices. As it may be easily seen from equation (11)

$$\mathbf{u} = \mathbf{C}\,\mathbf{x} \tag{21}$$

where $\mathbf{u}$ and $\mathbf{x}$ are column vectors. In the case of adjusting, the corresponding element of the matrix is $|\,\varepsilon_{ij}\,| = 1$, in the opposite case this value is zero.

If $\mathscr{T} = \mathscr{F}$ and the molecule contains N atoms, then $\mathbf{C}$ is of $(\mathrm{N}-1, \mathrm{N})$ order. If the number of faces in it is q, then the matrix is of $(\mathrm{N}-1+\mathrm{q}, \mathrm{N})$ order.

If the molecule is considered as a rigid structure then the set $\mathscr{R}$ of symmetry operators $\hat{\mathbf{R}}$ on the graph of the molecule may be interpreted in the following way. Let us account the subgraphs of the graph $\mathscr{G}$ having the properties

$$\underset{(i=1,2\ldots)}{x_i \in \mathscr{A}_\alpha \to \hat{\mathbf{R}}_k\, x_i \notin \mathscr{A}_\alpha} \qquad (\hat{\mathbf{R}}_k \in \mathbf{R}, \mathscr{A}_a \in \mathscr{G}) \tag{22}$$

and

$$u_{ij} \in \mathscr{A}_\alpha \to \hat{\mathbf{R}}_k\, u_{ij} \notin \mathscr{A}_\alpha \tag{23}$$

When Equations (22) and (23) are written for a symmetry operator $\hat{\mathbf{R}}_k$, the graph is divided into $\mathscr{A}_\alpha$ subgraphs and supplementary graph $\mathscr{A}/\mathscr{G}$ (where $\mathscr{A} = \bigcup\limits_{\alpha} \mathscr{A}_\alpha$). Subgraphs $\mathscr{A}_\alpha$ and $\mathscr{A}_\beta$ for which

$$\hat{\mathbf{R}}_k \mathscr{A}_\alpha = \mathscr{A}_\beta \tag{24}$$

are equivalent with respect to the operation $\hat{\mathbf{R}}_k$.

The

$$\mathscr{X}_i = \cup\, \hat{\mathbf{R}}_k\, x_i \qquad \mathscr{X}_i \subseteq \mathscr{X} \tag{25}$$

set is called an equivalent atomic set of the molecule. In the case when

$$\hat{\mathbf{R}}_k \hat{\mathbf{\Gamma}} x_i = \hat{\mathbf{\Gamma}} \hat{\mathbf{R}}_k\, x_i \tag{26}$$

there are equivalent valence line sets too:

$$\mathcal{U}_{ij} = \bigcup_{k} \hat{\mathbf{R}}_j \, \mathbf{u}_i \quad \mathcal{U}_{ij} \subseteq \mathcal{U} \tag{27}$$

The graph of the molecule may be divided into equivalent atomic sets which are disjunct to each other, *i.e.* into equivalent valence lines disjuncted to each other by choosing only single representatives of each set (i) and (i, j), respectively;

$$\bigcap_{i} \mathcal{X}_i = \varnothing \tag{28}$$

$$\bigcap_{(ij)} \mathcal{U}_{ij} = \varnothing \tag{29}$$

The quantity

$$\check{x}_i = \frac{1}{\mathrm{n}_i} \sum_{r=1}^{n_i} x_r \quad x_r \in \mathcal{X} \tag{30}$$

is called a symmetry atom (symmetry vertex) where n_i is the number of elements in the set $\mathcal{X}$; represented by x_i. The quantity

$$\check{u}_{ij} = \sum_{(pq)=1}^{m_{(ij)}=m_\gamma} u_{pq} \quad u_{pq} \in \mathcal{U}_{ij} \tag{31}$$

shall be called a symmetry line (symmetry arc) in which $m_{pq} = m_\gamma$ is the number of elements of the set $\mathcal{U}_{ij}$ represented by u_{ij}.

In this way the column vectors of Equation (21) are transformed into the following column vectors (if $\check{\mathbf{x}}$ is of dimension r)

$$\check{\mathbf{x}} = \begin{bmatrix} \overbrace{\frac{1}{n_1} \, \frac{1}{n_1} \cdots \frac{1}{n_1}}^{n_1 \text{ times}} \cdots 000 \cdots 0 \quad 0 \cdots 0 \\ \vdots \\ 0 \quad 0 \cdots 0 \quad \cdots 000 \cdots \underbrace{\frac{1}{n_r} \, \frac{1}{n_r} \cdots \frac{1}{n_r}}_{n_r \text{ times}} \end{bmatrix} \check{\mathbf{x}} = \mathbf{W} \cdot \check{\mathbf{x}} \tag{32}$$

and (if $\check{\mathbf{u}}$ is of dimensions s) respectively:

$$\check{\mathbf{u}} = \begin{bmatrix} \overbrace{1 \; 1 \cdots 1}^{m_1 \text{ times}} \cdots 000 \cdots 00 \cdots 0 \\ \vdots \\ 0 \; 0 \cdots 0 \cdots 000 \cdots \underbrace{11 \cdots 1}_{m_s \text{ times}} \end{bmatrix} \mathbf{u} = \mathbf{Q} \cdot \mathbf{u} \tag{33}$$

Taking into account Equations (32) and (33) Equation (21) is modified to

$$\check{\mathbf{u}} = \mathbf{Q}\,\mathbf{C}\,\mathbf{x} = \mathbf{S}\,\check{\mathbf{x}} \tag{34}$$

where **S** is a reduced order structural matrix accountig for the symmetry: *i.e.* the symmetry structural matrix.

Examples

Water (H_2O) point group $\mathbf{C}_{2v}$ (Fig. 2)
The matrix **C** for water is

$$\begin{array}{c|ccc} & H_1 & H_2 & O \\ \hline l_1 & 1 & 0 & 1 \\ l_2 & 0 & 1 & 1 \end{array}$$

The equivalent subgraphs for the symmetry operator $\hat{\mathbf{C}}_2$ are:

$$\mathscr{A}_1 = \{H_1\,l_1\};\ \mathscr{A}_2 = \{H_2\,l_2\};\ \mathscr{A}/\mathscr{G} = \{O\}$$

The symmetry atom is $\frac{1}{2}\,(H_1 + H_2)$
The symmetry line is $(l_1 + l_2)$
After transformation the following symmetry structural matrix is obtained

$$\begin{array}{c|cc} & \frac{1}{2}(H_1 + H_2) & O \\ \hline l_1 + l_2 & 1 & 2 \end{array}$$

Benzene (C_6H_6 point group $\mathscr{D}_{6h}$ (Fig. 3)]

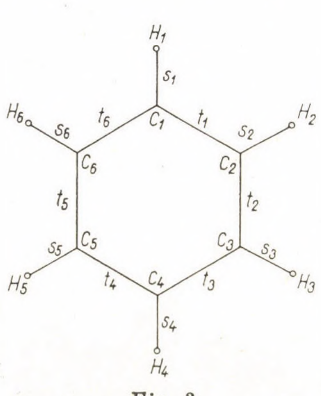

Fig. 3

The matrix **C** for benzene is

$$\begin{array}{c|cccccccccccc}
 & C_1 & C_2 & C_3 & C_4 & C_5 & C_6 & H_1 & H_2 & H_3 & H_4 & H_5 & H_6 \\
\hline
t_1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_2 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_3 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_4 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_5 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
t_6 & 1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_1 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
s_2 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
s_3 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
s_4 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
s_5 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
s_6 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1
\end{array}$$

The equivalent atomic sets for the symmetry operator $\hat{\mathbf{C}}_6$ are:

$$\mathcal{A}_1 = \{C_6t_6C_1s_1H_1\} \quad \mathcal{A}_2 = \{C_1t_1C_2s_2H_1\} \quad \mathcal{A}_3 = \{C_2t_2C_3s_3H_3\}$$

$$\mathcal{A}_4 = \{C_3t_3C_4s_4H_4\} \quad \mathcal{A}_5 = \{C_4t_4C_5s_5H_5\} \quad \mathcal{A}_6 = \{C_5t_5C_6s_6H_6\}$$

The symmetry atoms are $\frac{1}{6}(C_1 + C_2 + C_3 + C_4 + C_5 + C_6)$

$$\frac{1}{6}(H_1 + H_2 + H_3 + H_4 + H_5 + H_6)$$

The symmetry lines are: $(t_1 + t_2 + t_3 + t_4 + t_5 + t_6)$

$$(s_1 + s_2 + s_3 + s_4 + s_5 + s_6)$$

After transformation the following symmetry structural matrix **S** is obtained:

$$\begin{array}{c|cc}
 & \frac{1}{6}(C_1 + C_2 + C_3 + C_4 + C_5 + C_6) & \frac{1}{6}(H_1 + H_2 + H_3 + H_4 + H_5 + H_6) \\
\hline
t_1 + t_2 + t_3 + t_4 + t_5 + t_6 & 2 & 1 \\
s_1 + s_2 + s_3 + s_4 + s_5 + s_6 & 1 & 1
\end{array}$$

Conclusions

As shown by the above examples the application of symmetry operators considerably simplifies the structural matrix which may correspond reversibly to the geometrical configuration of the molecule. The correlation structure fixed by the structural matrix provides a possibility of the algebraic treatment of molecular configurations. The structural symmetry matrixes define uniquely the geometry of the molecule with the length of a representative of each equivalent sets of lines and with the angle between neighbouring lines.

With the aid of symmetry structural matrices the geometrical (bond) structure of the molecule may be put into electronic computers, which is necessary for the calculation of WILSON's **G** matrix used in calculation of molecular vibrations. The application of these conclusions will be dealt with in another communication.

SUMMARY

It has been found that the molecule as a geometric formation may be treated as a graph. Various quantities and functions were defined on this graph. A topological distinction was made among the different types of molecules, such as molecules with central, chain, planar cyclic and spatial cyclic structures. A definition is given for the structural matrix of the molecule. The conceptions of symmetry atom and symmetry line are introduced. The application of these conceptions results in a considerably simpler structural matrix. The symmetry structural matrix is suitable for the input of the molecular structure into electronic computers.

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THE REACTION OF 2-OXO-5,5-DI(ETHOXY)- AND 2-OXO-5,5-ETHYLENEDIOXY-CYCLOHEXANECARBOXYLIC ESTERS WITH BROMINE, N-BROMOSUCCINIMIDE AND SELENIUM DIOXIDE

A NOVEL AROMATIZATION REACTION

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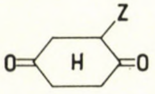
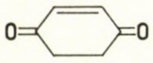
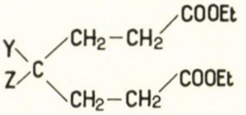
The monobromo (**Ib**) or monohydroxy derivative (**Ic**) of 1,4-cyclohexanedione (**Ia**) (or of some substituted derivative of it) was needed as the starting material for planned syntheses. However, treatment of **Ia** with 1 mole of bromine in chloroform solution gave hydroquinone even at 0°, instead of the expected **Ib**. Similarly, oxidation of **Ia** with selenium dioxide in dioxane also yielded hydroquinone instead of the desired **Ic**.



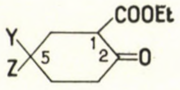
I



I



III



IV

a: Z=H
b: Z=Br
c: Z=OH

a: Y + Z=O
b: Y=Z=EtO
c: Y + Z = $-O-C_2H_4-O-$

In these two reactions hydroquinone is probably formed by isomerization [1] (cf. [2] and [11]) of the non-isolated intermediate, 2-cyclohexene-1,4-dione (**II**) [1], which, in turn, is derived from **Ib** or **Ic** by elimination of hydrogen bromide, and water, respectively.*

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* According to literature, **Ia** is oxidized to quinone by sulphuric acid and manganese dioxide, and even by ferric chloride [3], *i.e.*, a product of higher state of oxidation is formed than in our experiments. Products of the same oxidation state, p-dichlorobenzene [4], and hydroquinone diacetate [5], are formed, on the other hand, from **Ia** by the action of phosphorus pentachloride, and acetic anhydride, respectively; in the latter case the reaction is performed in the presence of sulphuric acid or toluene-sulphonic acid, and the former or atmospheric oxygen causes the oxidation. On the other hand, again according to literature, diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate is transformed by bromine in carbon disulphide solution into diethyl 2,5-dihydroxyterephthalate [17].

It seemed reasonable to attempt avoiding this undesirable aromatization by protection of *one* of the carbonyl groups of **Ia** by means of ketal formation, prior to bromination or oxidation. Although the monoethylene ketal of **Ia** may be prepared by its treatment with ethylene glycol [6, 9, 10], we rather started our experiments with the structurally related 5-monoketals of diethyl 2,5-dioxocyclohexanecarboxylate (**IVa**), *viz.* with the ethyl (**IVb**) and the ethylene ketals (**IVc**).

In these compounds, namely, the carbethoxy group can be expected to enhance the readiness of C-1 towards bromination and oxidative hydroxylation *i.e.*, to make selective substitution at C-1 easier; on the other hand, it should be possible to remove it subsequently by hydrolysis followed by decarboxylation. **IVc** can be prepared, according to literature [8, 10], in a relatively simple manner by DIECKMANN cyclization of the ethyleneketal (**IIIc**) [8, 9] of diethyl 4-ketopimelate (**IIIa**) [7, 8], which, in turn, is conveniently obtainable from 2-(2-furyl)-acrylic acid;* the diethyl ketals **IIIb** and **IVb** have been so far unknown.**

Literature data on the physical constants of **IIIc** are contradictory, the following values being given b.p.$_{0.3}$ 134°, $n_D^{25} = 1.4463$; b.p.$_{0.7}$ 127°, $n_D^{25} = 1.4486$ [8]; and b.p.$_{0.3}$ 115-6°; $n_D^{19} = 1.4480$ [9]. This shows that, at least in one case, the compound obtained was not pure **IIIc**.

As the ease of cyclization of **IIIc** depends to a large extent on the purity of the starting material [8], we tried to obtain **IIIc** of maximum purity and, using a semimicro spinning band rectification apparatus [12]*** — although at the expense of considerable tarring — we prepared **IIIc** 99.5% pure according to gas chromatographic analysis and contaminated only by 0.5% of **IIIa.** The physical constants of this product are: b.p.$_1$ 148°; $n_D^{20} = 1.4489 - 1.4495$; $n_D^{25} = 1.4474$.

DIECKMANN condensation [8] of this purified **IIIc** gave a 69% yield of pure **IVc** (m. p.: 49—51°) which crystallized immediately; whereas literature reports yields of 54% of non-crystalline, or of after long standing partly crystallizing [8], and of 32% of crystalline product (m. p.: 52—53°) [10], respectively.

According to its infrared spectrum **IVc** exists in crystalline form as the enol (**Vc**) stabilized by chelation (at least 95% enol content).

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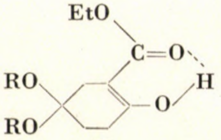
* The methyl esters may be similarly prepared [11].

** Experiments had been made to prepare the corresponding methyl esters, but a satisfactory purification of dimethyl 4,4-diethoxypimelate could not be achieved; from the crude product no cyclohexane derivative was formed under the conditions of the DIECKMANN cyclization [11].

*** Separation was effected in the *Laboratories of the Hungarian Research Institute for Mineral Oil and Natural Gas, Veszprém.* The authors wish to express their thanks here to the director of the Institute, academician Dr. M. FREUND and to the leader of the Analytical Section, Dr. E. KERÉNYI.

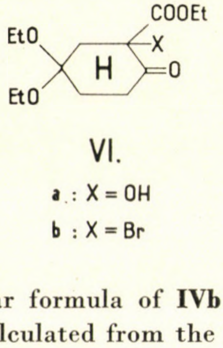


V

b: R=R′=Et
c: R + R′ = $-CH_2-CH_2-$

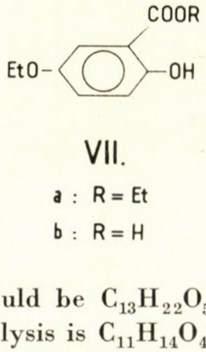
The diethyl ketals **IIIb** and **IVb** could not be prepared in perfectly pure state; since, according to literature, preparation of the corresponding methyl ester diethyl ketals does not lead to a homogeneous product either [11], it seems that the reason for this failure is the strongly diminished stability (*cf.* [13]) of "open" ketals compared with that of cyclic ethylene ketals.

Although the diethyl ketal **IVb** was not homogeneous, its reactions were examined with selenium dioxide in dioxane solution, and with N-bromosuccinimide in carbon tetrachloride, as well as with bromine in benzene solution. In all three cases the *same halogen-free substance* was obtained, and this fact alone shows that — contrary to our expectations — even in these cases the reaction was not simple substitution leading to **VIa** and **VIb**, respectively. Analytical data of the reaction product indicated a more profound decomposition. (The molecular formula of **IVb** would be $C_{13}H_{22}O_5$, while that of the reaction product calculated from the analysis is $C_{11}H_{14}O_4$.) The nature of the decomposition could be infered from the infrared and ultraviolet spectra of the reaction product. It unequivocally proved to be ethyl 5-ethoxysalicylate (**VIIa**); this conclusion was substantiated by alkaline hydrolysis of the compound yielding the known [14] 5-ethoxysalicylic acid (**VIIb**).



VI.

a : X = OH
b : X = Br

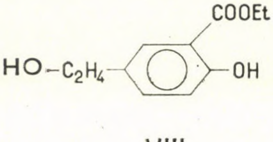


VII.

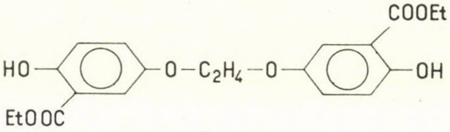
a : R = Et
b : R = H

Thus, **IVb** or the corresponding enolic form **Vb** is aromatized similarly to **Ia** under the given reaction conditions, and, therefore, our goal could not be reached even by preliminary ketal formation. The only difference is that now the intermediate, formed possibly analogously to **II**, is converted into the end-product by the elimination of ethanol instead of simple enolization.

The reaction of **Vc** with bromine in chloroform solution led to a similar but even more surprising result. Based on analogy, formation of **VIII** was expected, and the ultraviolet spectrum of the product was consistent with this structure, but the analytical data and the infrared spectrum were contradictory.

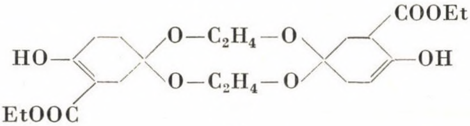


VIII.



IX.

However, structure **IX** corresponds to both the analytical data and to the two kinds of spectra, furthermore it could be proved by an unambiguous synthesis. Accordingly, **Vc** behaves in the reaction examined as if it had been first dimerized to **X**. Molecular weight determination, however, verified that really we had "monomeric" **Vc** in our hands.



X

Experimental*

Dehydrogenation of 1,4-cyclohexanedione

(*a*) A chloroform solution of 0.30 ml (5.5 mmole) of bromine was added dropwise – under ice-cooling and stirring – to the solution of 0.60 g (5.3 mmole) of **Ia** in 15 ml of dry chloroform. The mixture was allowed to stand for one or two days, and the separated brownish crystals (0.5 g; 84%) were filtered off with suction; m. p. and mixed m. p. with authentic hydroquinone: 170–172° (from ethyl acetate – chloroform).

(*b*) **Ia** (2.24 g, 20 mmole) was refluxed with 1.2 g (11 mmole) of selenium dioxide for 2 hrs. in 15 ml of dry dioxane; the solution, obtained by filtration with suction from the selenium-containing precipitate after cooling, was evaporated to dryness in vacuo. The residue was dissolved in methanol, treated with decolourizing carbon, again evaporated to dryness, and finally recrystallized from benzene to give 0.3 g of hydroquinone, m. p. and mixed m. p. with an authentic sample: 170–171°.

Ethyl 2-oxo-5,5-ethylenedioxycyclohexanecarboxylate (IVc)

IIIc purified on a spinning bond column [12] was used for the Dieckmann cyclization [8, 10]. The compound was cyclized in ethereal solution with sodium ethylate. Distillation under reduced pressure of the oily product, as described in the literature [8], was not necessary since the compound solidified to crystals on standing two days in a refrigerator. Yield: 68.6%, m. p.: 48–51° (from petroleum ether); lit. m. p. [10]: 52–53°.

$C_{11}H_{16}O_5$ (228.3)		
Calcd.	C 57.88	H 7.07
Found	C 58.14	H 6.98
	57.90	6.99%

Molecular weight (Rast method): 210, 252

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*All reported melting points are uncorrected.

Infrared spectrum (liquid film): ν O—H: not significant owing to chelation, and manifested only in the lowering of the base-line; ν C—H: 2990 and 2910; ν C=O: 1750 and 1725 (weak; ester and ketone band of the keto-ester tautomeride), 1660 (band of chelated ester group of the enol ester tautomeride); ν C=C: 1620 (conjugated, in chelate ring); ν C—O (enol, ester, ketal): 1300, 1235, 1205, 1160, 1125, 1070, 1030, 1005; γ O—H: 835 cm^{-1}.

The same product was prepared also starting from not quite pure **IIIc**, but here the product crystallized much more slowly, and the yield was considerably lower.

1,2-Bis-(3-ethoxycarbonyl-4-hydroxyphenoxy)-ethane (IX)

(*a*) 0.14 ml (2.5 mmole) of bromine in 0.5 ml of dry chloroform was added dropwise under ice-cooling and shaking to 0.57 g (2.5 mmole) of **IVc** dissolved in dry chloroform (1 ml); some crystallization started. The reaction mixture was heated to 30—40° for 30 minutes; next day it was evaporated to dryness and the residue recrystallized from ethanol. Yield: 0.25 g (52%) of **IX**, m. p.: 125—126° (from ethanol), colourless crystals.

$C_{20}H_{22}O_8$ (390.4)
Calcd. C 61.53 H 5.68
Found C 61.23 H 5.50
61.65 5.78%.

Ultraviolet spectrum (in ethanol): λ_{max} (log ε): 216 (4.71); 237 (4.19); 332 (3.94)

Infrared spectrum (in KBr pellet): ν O—H: 3245 (broad); ν C—H (aliphatic): 2995, 2950, 2910, 2885; ν C=O: 1685; aromatic skeletal vibrations: 1620, 1600, 1500, 1450 (?); ν C—O (phenol, ether, ester): 1285, 1225, 1180, 1085, 1050, 1025; γ C—H (aromatic) + ν C—C: 880, 835, 790; γ OH: 740 cm^{-1}.

(*b*) *Preparation of authentic* **IX.** Dry hydrogen chloride gas was passed into a solution of 0.20 g (0.58 mmole) of 1,2-bis-(3-carboxy-4-hidroxy-phenoxy)-ethane (see below) in anhydrous ethanol (20 ml) and the solution was refluxed for 4 hrs. Then it was evaporated to dryness, the residue taken up in another 20 ml portion of anhydrous ethanol, and boiling was continued for additional 4 hrs. with introducing hydrogen chloride gas; evaporation to dryness and treatment with hydrogen chloride in ethanol was then repeated once more. Cooling gave colourless crystals, (0.13 g; 57%) which were filtered off whith suction and washed with a small amount of ethanol; m. p.: 125—6° (from ethanol). No depression of the m. p. was observed in admixture with the substance prepared according to (*a*). The infrared spectra of the products obtained by the two methods were also identical.

1,2-Bis-(3-carboxy-4-hydroxyphenoxy)-ethane

A mixture of 3.10 g (15 mmole) of gentisic acid trihydrate, 2.0 g (10.5 mmole) of ethylene bromide, 2.3 g (41 mmole) of KOH, 15 ml of ethanol and 1 ml of water was refluxed for 6 hrs. After cooling, the solution was acidified with 10% hydrochloric acid, and evaporated to dryness in vacuo; the residue was taken up in boiling alcohol, treated with decolourizing carbon and the product precipitated by the addition of water. Yield: 0.30 g (18%) of a colourless crystal powder, m. p.: 288° (decomp.), that remained unchanged on further recrystallization from aqueous ethanol.

$C_{16}H_{14}O_8$ (334.3)
Calcd. C 57.49 H 4.22
Found C 57.57 H 4.40%.

Infrared spectrum (KBr pellet): ν OH (carboxylic acid dimer): 3300—2400 (phenolic OH and the various CH stretching vibrations hidden); ν C=O: 1665; aromatic skeletal vibrations: 1620, 1600, 1495, 1440 (?); δ CH_2: 1485; ν C—O: 1260, 1230, 1050; γ OH: 870 (acid), 785 (phenol); γ CH (aromatic) + ν C—C: 830, 805, 770 cm^{-1}.

Fractional evaporation of the mother liquor gave first 0.5 g of a mixture which was not further examined, and subsequently 1.5 g (48.5%) of unchanged gentisic acid.*

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* The procedure used was analogous to that described [15] for the preparation of ethylene glycol *bis*-(4-hydroxyphenyl)-ether. The structure of the reaction product is based on the fact, that gentisic acid, when reacted with ethylene bromide, is similarly alkylated on the hydroxy group at position 5 only [14]; furthermore, esterification of the product gave a compound which could also be prepared from **IVc**. In the course of the preparation of the product, we were satisfied with the poor yields obtained in the informative experiment, and no efforts were made to improve the yield.

Diethyl 4,4-diethoxypimelate (IIIb)*

Into the mixture of 11.5 g (0.05 mole) of diethyl 4-ketopimelate (**IIIa**) [7, 8], 11.1 g (0.075 mole) of ethyl orthoformate and 40 ml of dry ethanol dry hydrogen chloride gas was introduced for 1—2 minutes; the mixture turned red and became warm. Next day it was neutralized with sodium ethylate in anhydrous ethanol, the solvent evaporated and the residue fractionated in vacuo.

Yield: 13.8 g (90%) of **IIIb**, b. p.$_{22}$ 183—184° **, n_D^{20}: 1.4420; colourless liquid.

$C_{15}H_{23}O_6$ (304.3)

Calcd.	C 59.19	H 9.27
Found	C 59.16	H 8.89
	59.32	9.43%.

According to its infrared spectrum the product was, in spite of its narrow boiling range and correct analysis, not homogeneous,

Ethyl 2-oxo-5,5-diethoxycyclohexanecarboxylate (IV)***

2.3 g (0.1 g-atom) of sodium was placed into 100 ml of dry toluene; 30.4 g (0.1 mole) of not quite pure **IIIb**, obtained as previously described, was added dropwise within 1 hr. to the mixture heated in a bath of 100—115° with stirring. Stirring and heating was continued for 5 hrs. During this time the sodium dissolved, and the reaction mixture became brown. The solution was cooled to 0°, then either saturated with carbon dioxide in order to decompose the sodium salt, or slowly poured into 100 ml of 10% acetic acid cooled to 0°. The toluene solution was washed with water (when worked up with acetic acid, also with 10% sodium carbonate and finally with water again), dried and fractionated in vacuo. Yield: 10.5 g (41%) of **IVb**, b. p.$_{19}$ 150—153°; the compound is a colourless oil which solidifies in a refrigerator, and suffers rather rapid decomposition on standing.

$C_{13}H_{22}O_5$ (258.3)

Calcd.	C 60.44	H 8.59
Found	C 60.69	H 8.70
	60.81	8.33%.

The infrared spectrum of the product is very similar to that of **Vc**; consequently **IVb**, too, exists in the enolic form **Vb** in crystalline state; on the other hand, the spectrum indicated that our product was not quite homogeneous notwithstanding the narrow boiling range.

Ethyl 5-ethoxysalicylate (VIIa)

(*a*) 3.25 g (12.5 mmole) of not quite homogeneous **IVb**, prepared as described above, was refluxed for 2 hrs. in dry dioxane (15 ml) with 1.4 g (17.5 mmole) of selenium dioxide. The dark-red solution was filtered, evaporated to dryness in vacuo and the residue recrystallized from methanol. Yield: 0.7 g (27%) of initially brown, after repeated recrystallizations colourless crystals, m. p.: 64—67° (from methanol).

$C_{11}H_{14}O_4$ (210.2)

Calcd.	C 62.84	H 6.71
Found	C 62.85	H 6.64
	63.05	7.13%.

Molecular weight (SUCHARDA and BOBRANSKY method): 221, 251.
Ultraviolet spectrum (in ethanol): $\lambda_{\max}$ (log ε): 216 (4.41); 239 (3.87); 334 (3.67)
Gentisic acid (in 0.1 *M* HCl) [16]: 211 (4.49); 238 (3.97); 329 (3.72).

Infrared spectrum (KBr-pellet): ν OH: 3245 (broad); ν C—H (aliphatic): 2985, 2940, 2930, 2875; ν C=O: 1680; aromatic skeletal vibrations: 1620, 1595, 1495, 1450; ν C—O (phenol, ether, ester): 1290, 1225, 1180, 1080, 1050, 1020; γ C—H (aromatic) + ν C—C: 865, 840, 785; γ OH: 745. Data of *ethyl salicylate* for comparison: ν OH: 3200 (broad); ν C—H (aliphatic): 2955; ν C=O: 1685; aromatic skeletal vibrations: 1620, 1590, 1495, 1445; ν C—O (phenol, ester): 1310, 1255, 1220, 1160, 1145, 1090, 1035; γ C—H (aromatic) + ν C—C: 760, 700.

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* Regarding the failure of preparing the corresponding methyl ester, see [11].
** In an other experiment: bp$_{21}$: 167—8°.
*** Regarding the procedure, see [11].

(*b*) 1.49 g (5.8 mmole) of **IVb** was refluxed for 30 minutes in carbon tetrachloride (9 ml) with 1.33 g (7.5 mmoles) of N-bromosuccinimide; after cooling, the solution, which had a strong hydrogen bromide smell, was filtered from the separated succinimide, the filtrate evaporated to dryness, the residue taken up in petroleum ether, clarified, the solution evaporated again to dryness, and the residue recrystallized from methanol (12 ml).

Yield: 1.09 g (89.5%) of **VIIa**, m. p.: 67°.

(*c*) A solution of 0.28 ml (5.4 mmole) of bromine in benzene (10 ml) was added dropwise with shaking to the solution of 1.42 g (5.5 mmole) of **IVb** in 5 ml of dry benzene. After the evolution of hydrogen bromide had been completed, part of the product separated in crystalline form; the other part was obtained by evaporation to dryness of the filtrate and recrystallization of the residue from methanol.

Yield (total): 0.5 g (55%) of **VIIa**, m. p.: 67° (from methanol).

The products obtained according to (*a*), (*b*) and (*c*) gave no depression of the m. p. with another.

5-Ethoxysalicylic acid (VIIb)

0.59 g (2.8 mmole) of **VIIa** was allowed to stand at 30° for half an hour with 50 ml of 6% aqueous sodium hydroxide, the reaction mixture being shaken from time to time. In this way a clear yellowish solution was obtained which was cooled and acified. The separated colourless, light precipitate was filtered off by suction (0.50 g; 98%), m. p.: 160° (from aqueous methanol); lit. m. p. [14]: 164°.

$C_9H_{10}O_4$	(182.2)	
Calcd.	C 59.33	H 5.53
Found	C 59.60	H 5.57
	59.72	5.41%.

Infrared spectrum (KBr-pellet): ν OH: 3230 (weak; phenol), 3300—2400 (carboxylic acid dimer); ν C—H (aliphatic): 2980; ν C=O 1655; aromatic skeletal vibrations: 1620, 1600, 1495, 1460; δ CH_2: 1480; ν C—O: 1255, 1225, 1050; γ O—H: 900 (acid), 785 (phenol); γ C—H (aromatic) + ν C—C: 850, 800, 770.

Data of *salicylic acid* for comparison: ν OH: 3240 (weak; phenol), 3300—2400 (carboxylic acid dimer); ν C=O: 1660; aromatic skeletal vibrations: 1620, 1585, 1490, 1450 (?); ν C—O: 1255, 1160; γ O—H: 885 (acid), 785 (phenol); γ C—H (aromatic) + C—C: 760, 700.

The infrared spectra were determined by Dr. P. Sohár, the ultraviolet spectra by Dr. L. Láng; molecular weight determinations were carried out by Mrs. H. Medzihradszky-Schweiger, the microanalysises by Mrs. S. Viszt-Simon. The authors express here their grateful thanks for this assistance to their co-workers. Thanks are also due to Mrs. I. Börzsönyi and Mrs. F. Ilcsik, further to Mr. M. Kántor for the solution of the distillation problems and the gas chromatographic analyses.

SUMMARY

1,4-Cyclohexanedione (**Ia**) and its derivatives thus far investigated, *viz.* ethyl 5,5-diethoxy- (**IVb**) and 5,5-ethylenedioxy-2-oxo-cyclohexane carboxylate (**IVc**) become aromatized by treatment with elemental bromine, N-bromo-succinimide or selenium dioxide yielding thereby hydroquinone, ethyl 5-ethoxy-salicilate (**VIIa**) and 1,2-*bis*-(3-ethoxy-carbonyl-4-hydroxy-phenoxy)-ethane (**IX**), respectively.

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SYNTHETISCHE LINEARE POLYMERE, XXV*

ANNÄHERUNGSMETHODE ZUR BERECHNUNG DES SCHMELZPUNKTES VON SO_2-GRUPPEN ENTHALTENDEN POLYESTERN, POLYAMIDEN UND POLYÄTHYLENEN

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Einleitung

In früheren Mitteilungen [1—10] wurde gezeigt, daß zwischen dem Molekulargewicht einzelner Glieder von linearen polymerhomologen Reihen und solchen spezifischen Eigenschaften, die von additiven molaren Größen abgeleitet werden können, der folgende — auch mathematisch beweisbare — allgemeine Zusammenhang besteht:

$$\varphi_{sp} = \frac{a}{M} + b \tag{1}$$

φ_{sp} irgendeine »spezifische« Eigenschaft ist, z. B. $\frac{n^2-1}{n^2+2} \cdot \frac{1}{d}$ = spezifische Refraktion [1], n = Brechungsindex [2, 3], $\frac{v^{1/3}}{d}$ = spezifische Schallgeschwindigkeit [4], $\frac{\gamma^{1/4}}{d}$ = spezifisches Parachor [5], $-\frac{\gamma^{1/4}}{d}\log(n-1)$ = spezifisches Refrachor [5], $\frac{2{,}9 \log\log\eta}{d}$ = spezifische Viskositätszahl [5], $\frac{\varkappa}{d}$ = spezifische Suszeptibilität [5], $\frac{1}{d}$ = spezifisches Volumen [6], $\frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{1}{d}$ = spezifische Polarisation [7], $\frac{\bar{\mu}^2}{M}$ = spezifische Mitteldipolmomentquadrat [7], q = spezifische Verbrennungswärme [8], $\frac{1}{T}$ = Reziprokschmelzpunkt [9] usw. M ist das Molekulargewicht; a und b sind Konstanten und zwar gibt b den Zahlenwert der spezifischen Eigenschaft der Struktureinheit an — unabhängig davon ob es sich um lineare oder cyclische Polymere handelt [10] und a ist die Differenz zwischen den spezifischen Eigenschaften von Endgruppen und Struktureinheiten, multipliziert mit dem doppelten Molekulargewicht der Endgruppen. Die Konstante b kann zur Berechnung der

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* Synthetische lineare Polymere XXIV.: Faserforsch u. Textiltechn. **17,** 470 (1966).

Inkremente der Struktureinheit angewendet werden. Auf Grund dessen wurden einige — in der Literatur noch nicht angegebene — Inkremente für einige Atomgruppen ermittelt [2—5, 9].

Es wurde ferner an Dimethylpolysiloxan-Modellen gezeigt [11], daß der Wert der Konstante a von der Temperatur praktisch unabhängig ist, während der Wert der Konstante b eine Temperaturabhängigkeit aufweist. Weiterhin konnte gezeigt werden, daß die Gleichung (1) unter entsprechenden Versuchsbedingungen zur Molekulargewichtsbestimmung für Makromoleküle im Molekulargewichtsbereich von 10^3 bis 10^5 entwickelt werden kann, also für polymere Weichmacher, synthetische Fasern, wie Polyamid, Polyester usw. [1, 2, 4, 6].

Es wurde ferner darauf hingewiesen, [1, 5], daß bei genügend großem Molekulargewicht ($M \rightarrow \infty$) das Glied $\frac{a}{M}$ der Gleichung (1) vernachlässigt werden kann. In diesem Fall wird der Wert der spezifischen Eigenschaft allein durch den Wert der Konstante b bestimmt. Auf Grund dessen konnte der Schmelzpunkt von linearen Polyestern, Polyamiden Polyurethanen [12] sowie die Dichte und der Brechungsindex von Polyamiden [13], ferner die wahrscheinlichen Werte der spezifischen magnetischen Suszeptibilität und der spezifischen Schallgeschwindigkeit verschiedener Polymeren [13], berechnet werden.

Experimenteller Teil

In der vorliegenden Arbeit wurden die Schmelzpunkte der die SO_2 Gruppe enthaltenden Polyester, Polyamide und Polyäthylene auf Grund der schon früher angegebenen Methode [12] berechnet und mit den tatsächlich [14] gemessenen Schmelzpunkten verglichen. Grundlage der Berechnung der Schmelzpunkte war die folgende Gleichung (ähnlich zu [12]):

$$T_{Schmp,\,\infty} = \frac{M_k}{\sum_{i=1}^{n} \left(\frac{M}{T_{Schmp}} \right)_i}$$

wo $T_{Schmp,\infty}$ der vom Molekulargewicht schon unabhängige Schmelzpunkt des linearen Polymers, M_k das Molekulargewicht des Kettenmittelgliedes und $\left(\frac{M}{T_{Schmp}} \right)_i$ das »molare reziproke Schmelzpunktinkrement« der einzelnen Atomgruppen ist.

Zur Berechnung bzw. Bestimmung der Schmelzpunkte wurden die in Tab. I zusammengestellten »molaren reziproken Schmelzpunktinkremente« verwendet.

Tabelle I

Die zur Berechnung verwendeten »molaren Reziprokschmelzpunkt-Inkremente«

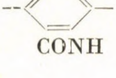
(CH_2) = 0,043
SO_2 = 0,046
COO = 0,113
 = 0,113
CONH = 0,056

Tabelle II

Berechneter und gemessener Schmelzpunkt von linearen Polyestern der allgemeinen Zusammensetzung

$$-[(CH_2)_z OOC(CH_2)_x SO_2(CH_2)_y SO_2(CH_2)_x COO]_n-$$

	x	y	z	T		Abweichung %
				gemessen	berechnet	
1	4	2	2	460,7	462,2	+0,3
2	4	2	4	457,2	449,6	—1,7
3	4	2	5	436,2	444,1	+1,8
4	4	2	6	439,7	439,2	—0,1
5	4	2	10	428,7	423,1	—1,3
6	5	2	2	459,7	449,6	—2,2
7	5	2	4	454,2	439,2	—3,4 (!)
8	5	2	6	433.2	430.2	—0.6
9	5	2	10	423,7	416,5	—1,7
10	3	4	2	459.7	462.2	+0.5
11	3	4	4	447,2	449,6	+0.5
12	3	4	5	429,7	437,6	+1,8
13	3	4	6	433,2	439,2	+1,3
14	3	4	10	422,2	423,1	+0.2
15	5	4	2	440.2	439.2	—0.2
16	5	4	4	428.7	430.4	+0.4
17	5	4	6	422,7	423,1	+0,1
18	5	4	10	413,7	410,3	—0,8
19	5	5	2	427,7	434,6	+1,6
20	5	5	4	425,2	426,5	+0,3
21	5	5	6	419,7	419,8	+0
22	5	5	10	407,7	408,4	+0,2
23	5	6	2	424,2	430,4	+1,4
24	5	6	4	418,7	423,1	+1,0
25	5	6	6	412,2	416,5	+1,0
26	5	6	10	404,2	406,0	+0,4
27	5	10	2	413,7	416,5	+0,7
28	5	10	4	411,7	410,3	—0,3
29	5	10	6	404,2	406,2	+0,4

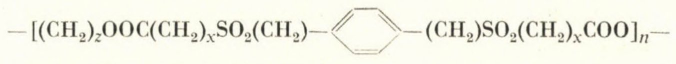
Die Berechnung dieser Inkremente erfolgte ähnlich wie in [12], indem die einzelnen Strukturelemente als Unbekannte betrachtet und im Verhältnis ihrer Vorkommenshäufigkeit in der Struktureinheit dem Quotienten des Molekulargewichtes der Struktureinheit und des in absoluten Graden ausgedrückten Schmelzpunktes der Verbindung gleichgesetzt wurden. Das Verfahren z. B. für die in Tab. II angeführten Verbindungen ist

$(CH_2 = x,\ SO_2 = y,\ COO = z)$:

$$12x + 2y + 2z = 0{,}8347$$
$$14x + 2y + 2z = 0{,}9024$$
$$15x + 2y + 2z = 0{,}9782 \text{ usw.}$$

Tabelle III

Berechneter und gemessener Schmelzpunkt von linearen Polyestern der allgemeinen Zusammensetzung



	x	z	T gemessen	T berechnet	Abweichung %
1	3	2	505,2	503,4	—0,4
2	3	4	487,2	487,5	+0,1
3	3	6	475,2	474,2	—0,2
4	3	10	455,7	453,4	—0,5
5	4	2	486,2	487,5	+0,3
6	4	4	477,2	474,2	—0,6
7	4	6	464,2	463,0	—0,3
8	4	10	449,2	445,0	—0,9
9	5	2	469,7	474,2	+1,0
10	5	4	462,7	455,7	—1,5
11	5	6	453,2	453,4	+0
12	5	10	446,2	437,7	—1,9

Das auf diese Weise erhaltene Gleichungssystem mit mehreren Unbekannten wurde mit der sog. Mittelwertsmethode gelöst. In Tab. I sind die so erhaltenen Inkremente zu sehen.

Die — auf Grund der in Tab. I angegebenen Inkremente — berechneten sowie die unmittelbar gemessenen Schmelzpunkte sind in den Tabellen II, III, IV und V angegeben.

Diskussion der Ergebnisse

Wie aus den Tabellen II, III, IV und V ersichtlich ist, zeigen die auf Grund der gegebenen Inkremente berechneten Schmelzpunkte (in den Tabellen sind die größeren prozentuellen Abweichungen mit ! bezeichnet) eine gute Übereinstimmung mit dem unmittelbar gemessenen. Die zwischen den berechneten und gemessenen Werten eventuell vorkommenden größeren oder kleineren Abweichungen können offenbar auf dieselbe Gründe zurückgeführt werden, wie die schon früher erwähnten [12]. Die Zahlenwerte der in der vorliegenden Arbeit angewandten Inkremente, verglichen mit den früher gebrauchten zeigen, daß obwohl die Schmelzpunkte als additiv betrachtet werden könnten, zur Zeit noch keine solchen universal brauchbaren Inkremente bestehen, die in Gegenwart der Struktureinheit von beliebiger Zusammensetzung ohne weiteres im allgemeinen verwendbar wären. Die Gegenwart einer bestimmten Atomgruppe beeinflußt die auf die anderen Atomgruppen bezüglichen Inkrementenwerte, und diese sind daher nur für die aus gegebenen Strukturelementen aufgebauten Polymeren oder deren Kombinationen gültig, doch kann sich ihr

Tabelle IV

Berechneter und gemessener Schmelzpunkt von linearen Polyamiden der allgemeinen Zusammensetzung

$$-[(CH_2)_zHNOC(CH_2)_5SO_2(CH_2)_ySO_2(CH_2)_5CONH]_n-$$

	y	z	T		Abweichung %
			gemessen	berechnet	
1	4	6	515,2	516,0	+0,2
2	4	10	510,2	487,5	−4,4 (!)
3	5	4	505,2	523,8	+3,7 (!)
4	5	5	485,2	516,0	+6,3 (!)
5	5	6	500,2	507,7	+1,5
6	5	10	496,2	481,6	−2,9
7	6	4	501,2	516,0	+2,9
8	6	5	483,7	507,8	+5,0 (!)
9	6	6	495,2	500,3	+1,0
10	6	10	492,2	476,1	−3,3 (!)
11	10	4	493,2	487,5	−1,2
12	10	5	475,2	481,6	+1,3
13	10	6	483,2	476,1	−1,5
14	10	10	481,7	457,9	−4,9 (!)

Tabelle V

Berechneter und gemessener Schmelzpunkt von linear Polyäthylensulfonen der allgemeinen Zusammensetzung

$$-[SO_2(CH_2)_ySO_2(CH_2)_z]_n-$$

	y	z	T		Abweichung %
			gemessen	berechnet	
1	4	6	516,2	514,2	−0,4
2	5	5	516,2	514,2	−0,4
3	6	4	516,2	514,2	−0,4

Alle gemessenen Schmelzpunkte sind der Arbeit von HORN [14] entnommen.

Wert ändern, wenn man von den schon vorhandenen Elementen das eine oder das andere ausläßt oder mit einem neuen vermehrt bzw. ersetzt (vergleiche Tabelle I und Tabelle I von [12]). Dies deutet darauf, daß bisher speziell bei den Berechnungen des Schmelzpunktes ein noch unbekannter Parameter noch nicht in Betracht gezogen bzw. vernachläßigt wurde. Dieser Parameter dürfte vermutlich für die Elementarzellen der aus verschiedenen Struktureinheiten aufgebauten Polymeren oder für die Kristallitgröße eventuell für die Kohäsionsenergie charakteristisch sein. Nur in Kenntnis des Wertes eines solchen

Parameters ist zu erwarten, daß die sich auf identische Gruppen beziehenden, im Zahlenwert verschiedenen Inkremente auf gleiche Werte transformiert werden können.

ZUSAMMENFASSUNG

Verfasser hat die schon früher von ihm angegebene [12] Methode zur Berechnung des Schmelzpunktes von Makromolekülen auf die SO_2-Gruppe enthaltende Polyester, Polyamide und Polyäthylene angewendet. Die berechneten Schmelzpunkte zeigten gute Übereinstimmung mit den gemessenen Werten. Die zur Berechnung erforderlichen molaren Reziprok-Schmelzpunkt-Inkremente hat Verfasser auf Grund der Angaben von Horn [14] bestimmt.

Der Vergleich dieser Inkremente mit den früher angegebenen ließ erkennen, daß der Inkrementenwert der aus verschiedenen Atomen bestehenden Struktureinheit auch durch die Gegenwart der übrigen Atomgruppen beeinflußt wird.

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Acta Chimica Academiae Scientiarum Hungaricae Tomus 51 (3), pp. 319—326 (1967)

INVESTIGATIONS ON DITHIOCARBAMATE FUNGICIDES

I THE PREPARATION OF N-CYANOALKYL AND N-CARBOXYALKYL DITHIOCARBAMATES

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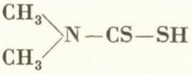
Among the agents used against the fungus diseases of agricultural crops (fungicides) the derivatives of dithiocarbamic acid are of prominent importance, especially the salts of dimethyl-(**I**) and ethylene-bis-dithiocarbamic acids (**II**).

These compounds, however, have mostly surface (contact) fungicidal activity only, and from the sprayed plant surface they cannot be absorbed by tissues to a considerable extent, thus they cannot ensure internal immunity against the pathogen by means of translocation with the fluid circulation.

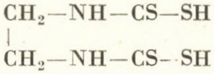
Several authors have tried to prepare compounds with internal therapeutic (systemic) fungicidal activity by incorporating into the molecule atomic groups which are supposed to act as carriers of the translocability, and at the same time ensure a hydrophilic/lipophilic ratio optimum for the effect. An analogy is offered by WAIN's statement [1], according to which one of the factors of activity in plant growth-regulating (auxinic) phenoxyalkyl carboxylic acids having good translocation capability is the presence of a carboxyl group, or such a group that can be converted into it; on the other hand, the surprising auxinic action of N,N-dimethyl-S-carboxymethyl-dithiocarbamate (**III**) prepared by VAN DER KERK [2] which indicates an analogy of systemic fungicidal and auxinic effects, showing that the structural requirements are partly similar.

Mainly starting with these considerations various authors have prepared carboxymethyl (**III, IV**) and carboxyethyl esters (**V, VI**) of dimethyl- and the ethylene-*bis*-dithiocarbamic acids (**I** and **II**, resp.) [2, 3, 4, 5, 6, 7, 8, 9], and during a research for growth-regulating agents, N-methyl-N-carboxymethyl-S-methyldithiocarbamate (**VII**) has also been synthesized [10].

Of these compounds, the salts of dimethyl- and ethylene-bis-dithiocarbamic acids(**I, II**) are very effective, while the carboxymethyl and carboxyethyl esters of acids (**III, IV, V, VI**) and the salts and S-methyl ester of N-methyl-N-carboxymethyldithiocarbamic acid (**VII**) have poor fungicidal activity. It means that the alternations made in order to improve the translocation capability markedly diminished fungicidal effectiveness.

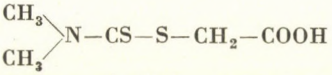


I

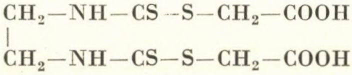


$$\begin{array}{l}CH_2{-}NH{-}CS{-}SH\\ |\\ CH_2{-}NH{-}CS{-}SH\end{array}$$

II

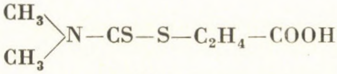


III

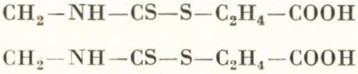


$$\begin{array}{l}CH_2{-}NH{-}CS{-}S{-}CH_2{-}COOH\\ |\\ CH_2{-}NH{-}CS{-}S{-}CH_2{-}COOH\end{array}$$

IV

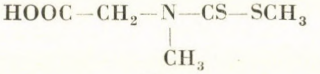


V



$$\begin{array}{l}CH_2{-}NH{-}CS{-}S{-}C_2H_4{-}COOH\\ CH_2{-}NH{-}CS{-}S{-}C_2H_4{-}COOH\end{array}$$

VI

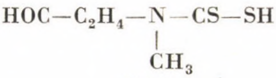


$$HOOC{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CS{-}SCH_3$$

VII

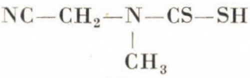
On basis of these results, appeared promising to prepare N-methyl-N-β-carboxyethyldithiocarbamic acid (**VIII**) and some of its derivatives; in this way it was hoped that the desired structural changes in dimethyldithiocarbamic acid ensuring translocation capability can be achieved. Similar structural alternations in the molecule of ethylene-*bis*-dithiocarbamic acid (**II**) were not attempted, because that would have involved removal of the hydrogen atom(s) attached to the nitrogen atom(s) which are, according to VAN DER KERK [11, 12] necessary for the activity of ethylene-*bis*-dithiocarbamates having a different mechanism of action.

The synthesis of the salts and several derivatives of N-methyl-N-cyanomethyldithiocarbamic acid (**IX**) and N-methyl-N-β-cyanoethyldithiocarbamic acid (**X**) was also thought reasonable, considering that they are converted into the above-mentioned N-carboxymethyl and N-β-carboxyethyl derivatives by enzymatic hydrolysis in the plant; so they can be regarded as the precursors of the latter compounds. The cyanoalkyl derivatives represent such substances whose initial lipophilic character changes during the transformation into a hydrophilic one, just as required for the processes of absorption and translocation.



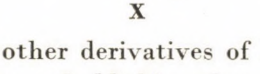
$$HOC{-}C_2H_4{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CS{-}SH$$

VIII



$$NC{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CS{-}SH$$

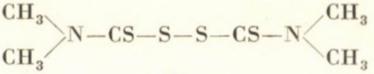
IX



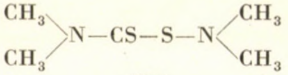
$$NC{-}C_2H_4{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CS{-}SH$$

X

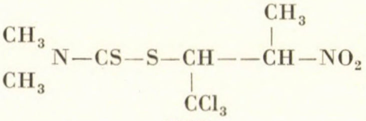
In the preparation of some other derivatives of N-methyl-N-β-carboxyethyl- (**VIII**) and N-methyl-N-β-cyanoethyldithiocarbamic acids (**X**) the analogy was considered to those reported derivatives of dimethyldithiocarbamic acid (**I**) which are known as the biologically most effective compounds. Such derivatives are tetramethylthiuram disulphide (**XI**), widely used as an agricultural fungicide, dimethylthiocarbamyldimethylsulphenamide (**XII**) [5], the previously mentioned N,N-dimethyl-S-carboxymethyldithiocarbamate (**III**) N,N-dimethyl-S-carboxyethyldithiocarbamate (**V**) [2, 3, 4, 5, 6, 7, 8, 9] and 1,1,1-trichloro-2-dimethylthiocarbamylmercapto-3-nitrobutane (**XIII**) [14].



XI



XII



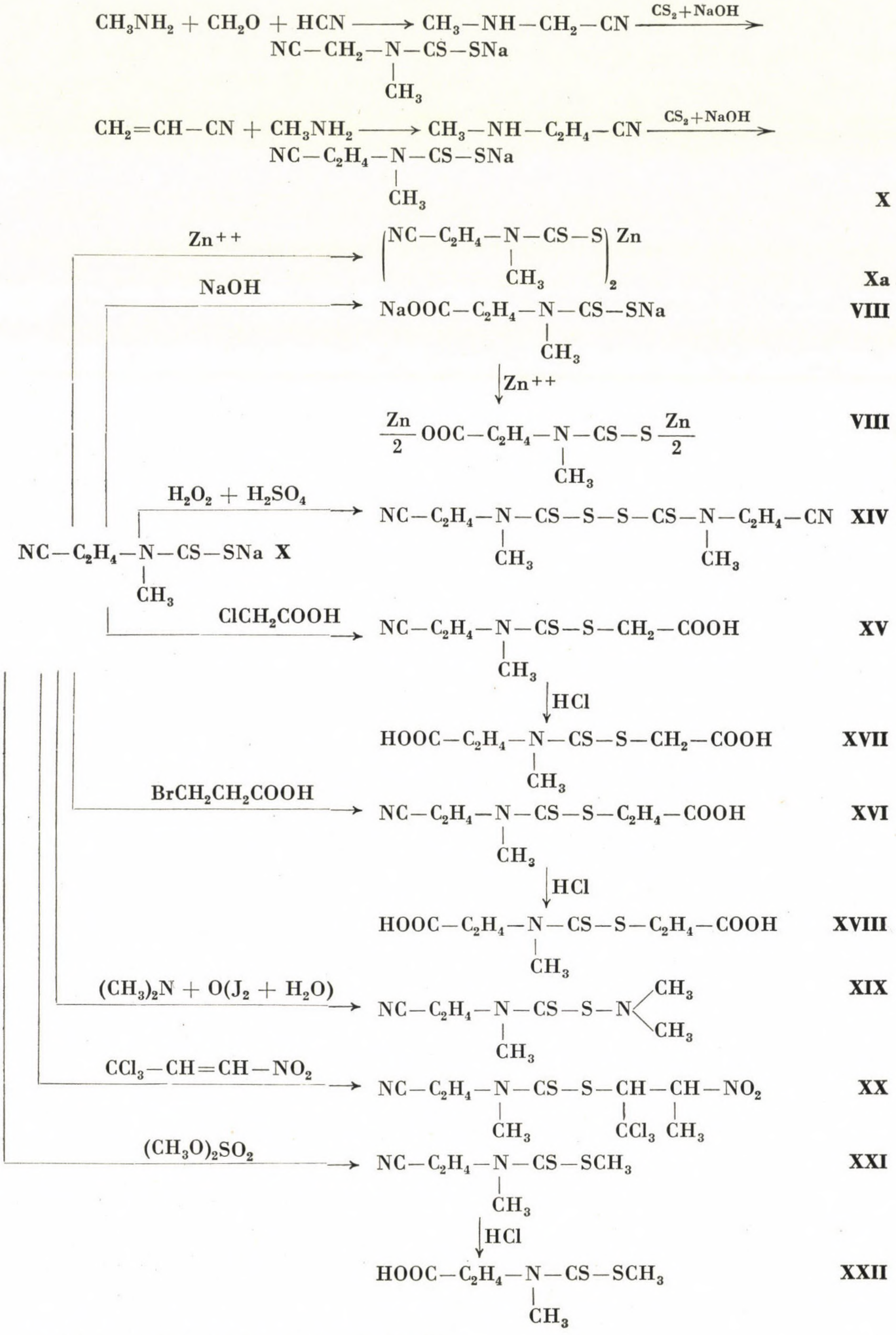
$(CH_3)_2N-CS-S-CH(CCl_3)-CH(CH_3)-NO_2$

XIII

The sodium salt and S-methyl ester (**VII**) of N-methyl-N-carboxymethyldithiocarbamic acid were prepared according to Rothwell and Wain [10] from glycine; the sodium salt of N-methyl-N-cyanomethyldithiocarbamic acid (**IX**) was made from methylaminoacetonitrile; and sodium salt of N-methyl-N-β-cyanoethyldithiocarbamic acid (**X**) from β-methylaminopropionitrile by reacting the compounds with carbon disulphide and sodium hydroxide in aqueous solution.

Disodium N-methyl-N-β-carboxyethyldithiocarbamate was prepared from the sodium salt of N-methyl-N-β-cyanoethyldithiocarbamic acid by alkaline hydrolysis, and from the product we synthesized the zinc salt, furthermore bis-(N-methyl-N-β-cyanomethyl)-thiuram disulphide (**XIV**) by oxidation with hydrogen peroxide and S-carboxymethyl ester (**XV**) and S-carboxyethyl ester (**XVI**) with monochloracetic acid and β-bromopropionic acid, respectively, in aqueous alkaline medium. On acid hydrolysis the latter two dithio esters gave the corresponding N-β-carboxyethyl derivatives (**XVII** and **XVIII**, resp.); these experiments utilized the surprising fact that while the salts of dithiocarbamic acids are fairly stable to alkalines but readily decomposed by acids, their esters are relatively sensitive to alkaline agents and show great stability in the presence of acids even under very energetic conditions[5]. Other compounds prepared in this work were N-methyl-N-β-cyanoethylthiocarbamyl-N′,N′-dimethylsulphenamide (**XIX**) made according to Pluijgers [5], and 1,1,1-trichloro-2-(methyl-β-cyanoethylthiocarbamylmercapto)-3-nitro-butane (**XX**) synthesized according to the method of Wain, Sobotka and Spencer [14]. It was impossible to transform the disulphide (**XIV**), the sulphenamide (**XV**) and the trichloronitrobutane (**XX**) derivatives into the corresponding N-β-carboxyethyl analogues either by acid or by alkaline hydrolysis, because decomposition of the compounds was in every case faster than the hydrolysis of the nitrile group.

Table I


CS$_2$+NaOH
CS$_2$+NaOH
X
Zn^{++}
Xa
NaOH
VIII
Zn^{++}
VIII
H$_2$O$_2$ + H$_2$SO$_4$
XIV
NC—C$_2$H$_4$—N—CS—SNa X
ClCH$_2$COOH
XV
HCl
XVII
BrCH$_2$CH$_2$COOH
XVI
HCl
XVIII
(CH$_3$)$_2$N + O(J$_2$ + H$_2$O)
XIX
CCl$_3$—CH=CH—NO$_2$
XX
(CH$_3$O)$_2$SO$_2$
XXI
HCl
XXII

Though simple alkalyne esters of dimethyldithiocarbamic acid are reported in the literature to be poor fungicides, N-methyl-N-β-cyanoethyl-S-methyldithiocarbamate (**XXI**) was also prepared in this work; its acid hydrolysis gave N-methyl-N-β-carboxyethyl-S-methyldithiocarbamate (**XXII**). Since this compound is the structural isomer of N,N-dimethyl-S-carboxyethyldithiocarabmate (**V**), a comparison of the biological activity of the two compounds was of interest.

The scheme of synthesizing the aforesaid compounds is shown in Table I.

Some of the prepared compounds may be considered to belong to the series of the various presumable biochemical transformation products of the cyanoalkyl derivatives. These substances have been prepared with the idea that an examination of their biological activity may allow conclusions as regards the course of the biochemical process in the plant.

The results of the investigations on the contact and systemic fungicidal effects of the compounds will be reported in forthcoming papers to be published elsewhere.

The authors wish to thank Miss G. Bruckner for the elemental analyses, Miss M. Tasnádi and Mrs. A. Marik for technical assistance during this work.

Experimental

Sodium N-methyl-N-β-cyanoethyldithiocarbamate (X)

To a solution of 20 g (0.05 mole) of sodium hydroxide and 264 ml of water 42 g (0.5 mole) of β-methylamino-propionitrile and, with cooling, 42 g (0.55 mole) of carbon disulphide were added. The mixture was shaken for 6 hrs. mechanically. During this time an almost homogeneous yellow solution resulted which was filtered and used directly for the further syntheses (25% solution).

Zinc N-methyl-N-β-cyanoethyldithiocarbamate (Xa)

To 7.3 g (0.01 mole) of the 25% solution of sodium-N-methyl-N-β-cyanoethyldithiocarbamate (**X**) 1.44 g (0.005 mole) of $ZnSO_4 \cdot 7H_2O$ dissolved in 10 ml of water was added. After short standing the precipitate was filtered off by suction washed with water until the effluent was free of sulphate, then with acetone; drying at 60° gave 1.9 g (100%) of a greyish-white amorphous powder, m. p. 208—210° (decomp.).

$C_{10}H_{14}N_4S_4Zn$. Calcd. S 33.38. Found S 33.9; 32.8%.

Zinc N-methyl-N-β-carboxyethyldithiocarbamate (VIII)

0.4 g (0.01 mole) of sodium hydroxyde was dissolved in 7.3 g (0.01 mole) of the 25% solution of **X**, the solution was refluxed until the evolution of ammonia ceased (for about 32 hrs.), and filtered. A concentrated aqueous solution of 3.1 g (0.011 mole) of $ZnSO_4 \cdot 7H_2O$ added, stirred for 10 minutes, filtered with suction, the precipitate washed with water, and dried. The product was purified by dissolving it in methanol; the solution was diluted with acetone, the precipitate filtered off, washed with water, and dried. 2 g (100%) of a white amorphous powder obtained that was soluble in methanol, but practically insoluble in water, benzene and chloroform; m. p. $> 300°$.

$C_5H_7NO_2S_2Zn$. Calcd. N 5.78; Zn 26.85. Found N 5.21; 5.34; Zn 26.43, 25.92%.

Bis-(N-methyl-N-β-cyanoethyl)-thiuram disulphide (XIV)

A mixture of 1.12 g of 30% hydrogen peroxide and 9.8 g of 10% sulphuric acid was added to 14.6 g (0.02 mole) of the 25% aqueous solution of **X** at 6—10° with stirring and cooling. Stirring was continued for an hour. The precipitated greenish, resinous product solidified on standing. It was filtered with suction, washed with water, dried, and recrystallized from absolute ethanol. Yield: 2.6 g (82%); m. p. 104—106°. The product was insoluble in water, cyclohexane and petrolether, soluble in benzene and ethanol.

$C_{10}H_{14}N_4S_4$. Calcd. N 17.61; S% 40.25. Found N 17.64; S 39.1; 40.4%.

N-Methyl-N-β-cyanoethyl-S-carboxymethyldithiocarbamate (XV)

2.4 g (0.06 mole) of sodium hydroxide in 6 ml of water was added to 36.4 g (0.05 mole) of the 25% solution of **X**, followed by 5.64 g (0.06 mole) of monochloroacetic acid in 10 ml of water. The solution was let to stand for 24 hrs. It was acidified with 10% hydrochloric acid to pH 3. The precipitated oil solidified in a few minutes. It was filtered off, washed with water, and recrystallized from water. Yield: 8.83 g (81%) of a white crystalline substance, m. p. 125°.

$C_7H_{10}N_2O_2S_2$. Calcd. S 29.35; N 12.84. Found S 29.0; 12.63, 12.40%. Neutr. equiv. 99.4; 96.8%.

N-Methyl-N-β-carboxyethyl-S-carboxymethyldithiocarbamate (XVII)

4.36 g (0.02 mole) of N-methyl-N-β-cyanoethyl-S-carboxymethyldithiocarbamate (**XV**) in 14 ml of concentrated hydrochloric acid was refluxed for 3 hrs. The clear warm solution deposited a copious crystalline precipitate on cooling; it was filtered off, washed with ice-cold water, and recrystallized from a little water. Yield: 2.2 g (46%) of a white crystalline product that was readily soluble in water, less in ethanol, insoluble in benzene and cyclohexane.

$C_7H_{11}NO_4S_2$. Calcd. N 5.91; S 27.0. Found N 5.53; 5.70; S% 26.54; 26.86%. Neutr. equiv. 100.7; 99.8%.

N-Methyl-N-β-cyanoethyl-S-β-carboxyethyldithiocarbamate (XVI)

A solution of 2.2 g (0.055 mole) of NaOH and 8.4 g (0,055 mole) of β-bromopropionic acid in 15 ml of water was added to 36.4 g (0.05 mole) of the 25% aqueous solution of **X**; after the spontaneous reaction had been completed, the mixture was refluxed for 1 hr. cooled, and acidified with 10% hydrochloric acid to pH 3. A brown oily product was obtained that soon solidified. It was filtered off, washed with water, and recrystallized from a 1 : 1 mixture of methanol and water. Yield: 8.85 g (76%) of a white crystalline product; m. p. 124°.

$C_8H_{12}N_2O_2S_2$. Calcd. N 12.17; S 27.60. Found N 12.34; S 27.52%.

N-Methyl-N-β-carboxyethyl-S-β'-carboxyethyldithiocarbamate (XVIII)

4.64 g (0.02 mole) of N-ethyl-N-β-cyanoethyl-S-β'-carboxyethyldithiocarbamate (**XVI**) in 14 ml of concentrated hydrochloric acid was refluxed for 3½ hrs. The mixture was cooled in a refrigerator, the precipitate filtered off, and recrystallized from a little water. Yield: 2.5 g (50%) of a white crystalline product m. p. 118—120°.

$C_8H_{13}NO_4S_2$. Calcd. C 38.05; H 5.18; N 5.58; S 25.42. Found C 38.18; H 5.22; N 5.77; S 25.18%. Neutr. equiv. 100.1; 100.1%.

N-Methyl-N-β-cyanoethylthiocarbamyl-N',N'-dimethylsulphenamide (XIX)

To the analogy of the method of PLUIJGERS [5], 63 g (0.55 mole) of 40% aqueous dimethylamine solution was added to 58 g (0.08 mole) of the 25% aqueous solution of **X**; then, with stirring and at room temperature, a solution made of 53 g of KI, 500 ml of water and 20.5 g iodine was introduced during 1½ hrs. Stirring was continued for another 1½ hrs; during this time a precipitate was formed, that was filtered off, washed with water, dried, and recrystallized from cyclohexane. Yield: 7.5 g (47%) of white crystals; m. p. 50—51°. The product is readily soluble in methanol and benzene, moderately in petroleumether and cyclohexane, and scarcely in water.

$C_7H_{13}N_3S_2$. Calcd. N 20.69; S 31.62. Found N 20.05; 20.33; S 31.17; 31.53%.

1,1,1-Trichloro-2-(N-methyl-N-β-cyanoethylthiocarbamyl-mercapto)-3-nitrobutane (XX)

To the analogy of the method of WAIN, SOBOTKA and SPENCER [14], 6.55 g (0.03 mole) of sodium-N-methyl-N-β-cyanoethyldithiocarbamate **(X)** (obtained by evaporating the aqueous solution) was dissolved in 70 ml of methanol. The solution was cooled to —5°, and at about this temperature a solution of 6.15 g of 1,1,1-trichloro-2-nitrobut-2-ene in 6 ml of methanol was added. The mixture allowed to stand 1 hr., poured into 300 ml of water, and acidified with glacial acetic acid. A reddish-brown, resinous product was obtained that solidified gradually.

Recrystallization from ethanol gave 7.8 g (71%) of greenish-yellow needles, m. p. 109—110°.

$C_9H_{13}Cl_3N_3O_2S_2$. Calcd. Cl 29.21; S 17.55. Found Cl 29.8; 29.1; S 17.51; 16.9%.

N-methyl-N-β-carboxyethyl-S-methyldithiocarbamate (XXII)

12.6 g (0.1 mole) of dimethyl sulphate was added to a mixture of 88 g (0.11 mole) of the 25% aqueous solution of **X** and 120 ml of water, with cooling and stirring at 32—35°. Stirring was continued for 1 hr. An oil was obtained that solidified on short standing. This crude N-methyl-N-β-cyanoethyl-S-methyldithiocarbamate **(XXI)** was filtered off and refluxed for 10 minutes with 70 ml of conc. hydrochlorid acid. Cooling gave an oil that became soon crystalline. It was filtered off and recrystallized from water to Yield 11 g (57%) of a white crystalline product, m. p. 94—96°.

$C_6H_{11}NO_2S_2$. Calcd. N 7.25; S 33.16. Found 7.43; 7.28; S 33.09%. Neutr. equiv. 100.1; 100.6%.

SUMMARY

The sodium salts of N-methyl-N-β-cyanoethyldithiocarbamic acid and of N-methyl-N-β-carboxyethyldithiocarbamic acid and some of their S-substituted derivatives were prepared by the authors with the scope to obtain new derivatives which, in addition **to** possessing a biological activity similar to that of dimethyl-dithiocarbamic acid derivatives applied in agriculture as fungicides, have simultaneously also a systemic effect. On starting from methyl-amino-propionitrile and carbon disulphide, the sodium salt of N-methyl-N-β-cyanoethyl-dithiocarbamic acid was prepared. The S-substituted derivatives of this compound were obtained analogously to the similar derivatives of dimethyldithiocarbamic acid. The carboxy radical has been developed by the subsequent hydrolysis of the cyano group.

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DERIVATIVES OF ALKOXYBENZOIC ACIDS, III

BASIC ESTERS OF 4-ALKOXY-3,5-DIMETHOXY- AND 2-ALKOXY-3,4-DIMETHOXYBENZOIC ACIDS WITH PAPAVERINE-LIKE SPASMOLYTIC ACTION

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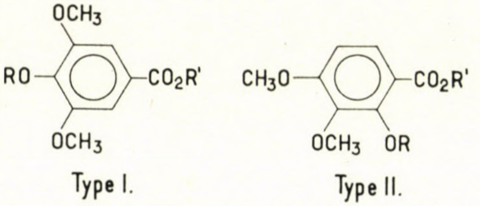
In our previous papers [1, 2] a novel group of central nervous system depressant alkoxybenzamides was reported. On basis of the results obtained, an investigation of other acid derivatives also seemed interesting.

Several papers have been published on the basic esters of 3,4,5-trimethoxybenzoic acid. The principal aim of these researches was the synthesis of tranquillizing and hypotensive agents, the 3,4,5-trimethoxybenzoyl group being an important part of reserpine. However, basic esters of benzoic acids containing longer alkoxy groups have attracted little attention so far [3]. In our present experiments, basic esters of 4-longer-alkoxy-3,5-dimethoxy- and 2-longer-alkoxy-3,4-dimethoxybenzoic acids (Types **I** and **II**) have been synthesized and examined.



R = alkyl; R′ = aminoalkyl group

Preliminary tests showed these esters to posses a spasmolytic action resembling papaverine. In order to study this action, several variations have been made in both the acid and alcohol parts of the esters. Changes made in the acid moiety were the following:

a) The length of the alkoxy group in positions 2 or 4, respectively, was changed;

b) A branched chain was introduced;

c) An unsaturated alkyl or cycloalkyl group was employed.

Variations in the basic alcohol part were the following:

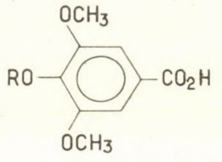
a) The substituents of the N atom were changed;

b) The distance between the 0 and N atoms was varied;

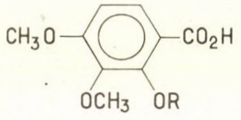
c) A branched chain was used.

Table I

Alkoxydimethoxybenzoic



Type I.



Type I.

Type	R	Method	Alkylating agent	Solvent	Reaction temperature, °C	Reaction time, hours	Yield, %
I	C_2H_5	A	$(C_2H_5)_2SO_4$	aceto-phenone	135—140	10	89
I	n-C_3H_7	B	n-C_3H_7Br	n-C_4H_9OH	117	15	73
I	$CH_2{=}CHCH_2$	B	$CH_2{=}CHCH_2Br$	CH_3OH	65	4	84
I	n-C_4H_9	A	n-C_4H_9Br	aceto-phenone	140—145	17	89
I	iso-C_4H_9	B	iso-C_4H_9J	n-C_4H_9OH	117	45	49
I	sec-C_4H_9	A	sec-C_4H_9Br + 0.2 mole NaI	aceto-phenone	140—145	18	43
I	n-C_5H_{11}	B	n-$C_5H_{11}Br$	n-C_4H_9OH	120—122	15	61
I		A	—Br	butanone	79	6	86
I	$CH_3OCH_2CH_2$	A	$CH_3OCH_2CH_2Br$ + 0.2 mole NaI	aceto-phenone	135—140	20	83
II	$CH_2{=}CHCH_2$	A	$CH_2{=}CHCH_2Br$	aceto-phenone	130—135	7	94
II	n-C_4H_9	A	n-C_4H_9Br	aceto-phenone	135—140	15	91

Data of salts of the basic esters prepared are summarized in Table II.

The pharmacological evaluation of 28 compounds permitted several observations concerning the relationship between chemical structure and spasmolytic action. Details of the pharmacological examinations will be published in *Acta Physiol. Hung.*; here the main features of the results are only summarized:

acids

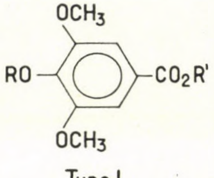
Recrystallization solvent	M. p., °C	Empirical formula	Molecular weight	Analysis, %				Notes
				Calcd:		Found:		
				C	H	C	H	
70% aqueous methanol	125—127	$C_{11}H_{14}O_5$	226.6	58.41	6.20	58.32	6.23	See ref. [4]
petroleum ether-ethyl acetate (3:1)	124—126	$C_{12}H_{16}O_5$	240.4	59.93	6.71	59.92	6.90	
petroleum ether-ethyl acetate (2:1)	122—124	$C_{12}H_{14}O_5$	238.7	60.48	5.88	60.41	5.93	Methyl ester, see ref, [5],
70% aqueous methanol	107—109	$C_{13}H_{18}O_5$	254.6	61.40	7.13	61.42	7.07	Methylester, m.p. 30-31°
70% aqueous methanol	123—125	$C_{13}H_{18}O_5$	254.6	61.40	7.13	61.52	7.13	
petroleum ether-acetone (9 : 1)	128—129	$C_{13}H_{18}O_5$	254.6	61.40	7.13	61.32	7.17	
petroleum ether-acetone (10 : 1)	93—95	$C_{14}H_{20}O_5$	268.6	62.60	7.50	62.46	7.65	
70% aqueous methanol	163—165	$C_{15}H_{18}O_5$	278.2	64.82	6.48	64.67	6.53	
water-ethanol (3 : 1)	109—111	$C_{12}H_{16}O_6$	256.6	56.25	6.25	56.14	6.19	
petroleum-ether acetone (2 : 1)	91—93	$C_{12}H_{18}O_5$	238.7	60.48	5.88	60.39	5.95	
70% aqueous methanol	82—83	$C_{13}H_{18}O_5$	254.6	61.40	7.13	61.52	7.22	

1. In general, basic esters of 4-longer-alkoxy-3,5-dimethoxybenzoic acids have a stronger spasmolytic action than those of 2-longer-alkoxy-3,4-dimethoxy-benzoic acids.

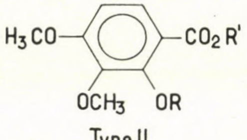
2. With the same acid component, 2-diethylaminoethyl and 2-N-pyrrolidinoethyl esters show the strongest spasmolytic action; peroral resorption of the latter group of compounds is more favourable.

Table II

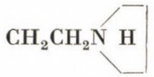
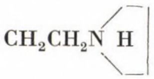
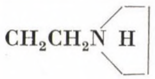
Salts of the basic esters of



Type I.

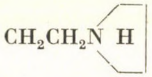
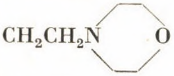
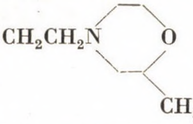
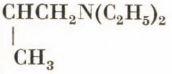
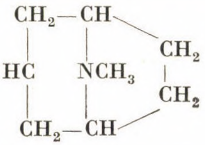
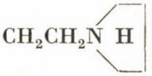
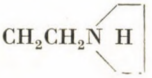


Type II.

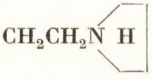
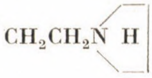
Compd. No.	Type	R	R'	Salt	Method	Recryst. solvent	M. p., °C
V—104	I	C_2H_5	$CH_2CH_2N(C_2H_5)_2$	hydro-chloride	C	acetone-isopropanol (10 : 1)	145—148
V—103	I	C_2H_5	 CH_2CH_2N H	hydro-chloride	C	acetone-isopropanol (4 : 1)	169—171
V—93	I	n-C_3H_7	$CH_2CH_2N(C_2H_5)_2$	hydro-chloride	C	acetone	147—149
V—94	I	n-C_3H_7	 CH_2CH_2N H	hydro-chloride	C	acetone	136—138
V—102	I	n-C_3H_7	$CH_2CH_2CH_2N(CH_3)_2$	hydro-chloride	C	acetone isopropanol (12 : 1)	140—141
V—73	I	$CH_2{=}CHCH_2$	$CH_2CH_2N(CH_3)_2$	hydrogen maleate	C	butanone	105—107
V—74	I	$CH_2CH_2N(CH_3)_2$	$CH_2CH_2N(CH_3)_2$	dihydro-chloride	C	ethanol-water (60 : 1)	207—209
V—136	I	$CH_2CH_2OCH_3$	 CH_2CH_2N H	hydro-chloride	C	acetone-ethanol (3 : 1)	146—149
V—76	I	n-C_4H_9	$CH_2CH_2N(CH_3)_2$	hydrogen maleate	C	butanone	87—88
V-75/A	I	n-C_4H_9	$CH_2CH_2N(C_2H_5)_2$	hydro-chloride	D	acetone-isopropanol (9 : 1)	137—139
V—77	I	n-C_4H_9	$CH_2CH_2N(iso\text{-}C_3H_7)_2$	hydrogen fumarate	C	ethanol	164—165

alkoxydimethoxybenzoic acids

Empirical formula	Molecular weight	Analysis, %								Notes
		Calcd.				Found				
		C	H	N	Cl	C	H	N	Cl	
$C_{17}H_{28}ClNO_5$	362.4			3.87	9.83			3.83	9.77	See ref. [3]
$C_{17}H_{26}ClNO_5$	360.4			3.88	9.88			3.84	9.79	
$C_{18}H_{30}ClNO_5$	376.4			3.73	9.45			3.81	9.38	
$C_{18}H_{28}ClNO_5$	374.4			3.74	9.48			3.77	9.41	
$C_{17}H_{28}ClNO_5$	362.4			3.87	9.83			3.90	9.79	
$C_{20}H_{27}NO_9$	425.6	56.55	6.35	3.30		56.58	6.41	3.36		
$C_{17}H_{30}Cl_2N_2O_5$	413.8			6.78	17.22			6.72	17.09	
$C_{18}H_{28}ClNO_6$	390.3			3.59	9.12			3.53	9.12	
$C_{21}H_{31}NO_9$	441.7	57.10	7.09	3.18		57.00	6.97	3.23		
$C_{19}H_{32}ClNO_5$	390.4			3.59	9.12			3.56	9.04	
$C_{25}H_{39}NO_9$	497.5	60.48	7.85	2.82		60.37	7.94	2.89		

Compd. No.	Type	R	R'	Salt	Method	Recryst. solvent	M. p., °C
V-80/A	I	n-C_4H_9		hydrochloride	C	ethyl acetate	122—124
V—79	I	n-C_4H_9		hydrogen maleate	C	acetone	117—118
V—78	I	n-C_4H_9		hydrochloride	C	acetone	181—183
V—84	I	n-C_4H_9		hydrochloride	C	acetone-ethanol (4 : 1)	182—183
V—105	I	n-C_4H_9	$CH_2CH_2OCH_2CH_2N(C_2H_5)_2$	dihydrogen citrate	C	acetone	82—85
V—90	I	n-C_4H_9	$CH_2CH_2CH_2N(CH_3)_2$	hydrochloride	C	butanone	139—141
V—106	I	n-C_4H_9	 $\underset{CH_3}{CH}CH_2N(C_2H_5)_2$	hydrochloride	C	acetone	148—150
V—83	I	n-C_4H_9		dihydrogen citrate	C	acetone-methanol (1 : 1)	162—163 (decomp.)
V—96	I	iso-C_4H_9	$CH_2CH_2N(C_2H_5)_2$	hydrochloride	C	acetone	153—154
V—95	I	iso-C_4H_9		hydrochloride	C	acetone	153—154
V—98	I	sec-C_4H_9	$CH_2CH_2N(C_2H_5)_2$	hydrochloride	C	acetone	152—153
V—97	I	sec-C_4H_9		hydrochloride	C	butanone	127—129

Empirical formula	Molecular weight	Analysis, %								Notes
		Calcd.				Found				
		C	H	N	Cl	C	H	N	Cl	
$C_{19}H_{30}ClNO_5$	388.4			3.61	9.16			3.63	91.12	Hydrogen maleate (compd. V-80) m. p. 108—110° (from ethyl acetate)
$C_{24}H_{35}NO_9$	481.6	59.75	7.12	2.91		59.63	7.18	3.03		
$C_{19}H_{30}ClNO_6$	404.2	56.50	7.48	3.47	8.81	56.65	7.61	3.38	8.73	
$C_{20}H_{32}ClNO_6$	418.2	57.45	7.66	3.35	8.53	57.33	7.80	3.41	8.51	
$C_{27}H_{43}NO_{13}$	589.5	55.05	7.31	2.38		54.92	7.42	2.33		
$C_{18}H_{30}ClNO_5$	376.4			3.73	9.45			3.91	9.31	
$C_{20}H_{34}ClNO_5$	404.4			3.47	8.81			3.41	8.75	
$C_{27}H_{39}NO_{12}$	569.2	56.81	6.91	2.46		56.67	7.03	2.51		
$C_{19}H_{32}ClNO_5$	390.4			3.59	9.12			3.71	9.17	
$C_{19}H_{30}ClNO_5$	388.4			3.61	9.16			3.54	9.09	
$C_{19}H_{32}ClNO_5$	390.4			3.59	9.12			3.65	9.07	
$C_{19}H_{30}ClNO_5$	388.4			3.61	9.16			3.57	9.09	

Compd. No.	Type	R	R′	Salt	Method	Recryst. solvent	M.p., °C
V—92	I	n-C_5H_{11}	$CH_2CH_2N(C_2H_5)_2$	hydrochloride	C	acetone	127—129
V—91	I	n-C_5H_{11}	 $CH_2CH_2N\ H$	hydrochloride	C	butanone-water (100 : 1)	124—125
V—112	I		$CH_2CH_2N(C_2H_5)_2$	hydrochloride	D	acetone	157—159
V—114	II	$CH_2CH{=}CH_2$	$CH_2CH_2N(C_2H_5)_2$	hydrochloride	C	acetone	93—95
V—99	II	n-C_4H_9	$CH_2CH_2N(C_2H_5)_2$	hydrochloride	C	butanone	107—109
	II	n-C_4H_9	 $CH_2CH_2N\ H$	dihydrogen citrate	C	butanone	83—85

3. In the alcohol part, the preferable distance between the N and O atoms is 2 carbon atoms. Resorption is improved, while spasmolytic action is decreased by a distance of 3 carbon atoms.

4. In the alcohol part, a straight carbon chain between the N and O atoms is more favourable than a branched chain.

In position 4 of the acid, the presence of a *n*-butyl or isobutyl group is advantageous. The action becomes stronger by introduction of an *n*-amyl group, but resorption is less. By introduction of an *n*-propyl group, resorption is improved, but the action is weakened.

Among the compounds investigated, 2-N-pyrrolidino-ethyl 4-*n*-butoxy-3,5-dimethoxybenzoate hydrochloride (compound V—80/A) has been found the most favourable in view of spasmolytic action, toxicity, and resorption; it is considered of sufficient interest to justify clinical trials.

One of the esters, compound V—104, has been reported in the meantime in the literature [3].

As the basic esters are oils, their crystalline, water-soluble salts have been used for the pharmacological tests. In general, the basic esters have been prepared from the acid chlorides with the appropriate amino alcohol or — in some cases — from the acid and the aminoalkyl chloride. All alcohols used are described in the literature except N-(2′-hydroxyethyl)-2-methylmorpholine which has been synthesized by condensing ethylene chlorohydrin with 2-methylmorpholine.

Empirical formula	Molecular weight	Analysis- %								Notes
		Calcd.				Found				
		C	H	N	Cl	C	H	N	Cl	
$C_{20}H_{34}ClNO_5$	404.4			3.47	8.81			3.46	8.72	
$C_{20}H_{32}ClNO_5$	402.4			3.48	8.83			3.39	8.77	
$C_{21}H_{32}ClNO_5$	414.5			3.38	8.61			3.35	8.53	
$C_{18}H_{28}ClNO_5$	374.4			3.74	9.48			3.79	9.38	
$C_{19}H_{32}ClNO_5$	390.4			3.59	9.12			3.66	9.14	
$C_{25}H_{37}NO_{12}$	543.2	55.31	7.03	2.58		55.22	7.14	2.53		

The acids have been prepared by alkylating methyl or *n*-butyl 4-hydroxy-3,5-dimethoxybenzoate or methyl 2-hydroxy-3,4-dimethoxybenzoate, respectively, by means of an alkyl halide, and hydrolyzing the 4-alkoxy or 2-alkoxy ester to the acid. The alkylation of methyl 4-hydroxy-3,5-dimethoxybenzoate may be accomplished either by the reaction of the ester with an alkylating agent and potassium carbonate in acetophenone (Method "A"), or with the sodium salt of the ester and an alkylating agent in an alcoholic solvent (Method "B"). For the alkylation of methyl 2-hydroxy-3,4-dimethoxy-benzoate the first method was only successful. The preparation of 4-(2′-dimethylaminoethoxy)-3,5-dimethoxybenzoic acid was somewhat different (see Experimental). 4-Ethoxy-3,5-dimethoxybenzoic acid had been known from literature [4]; methyl 4-allyloxy-3,5-dimethoxybenzoate had also been described [5]. Data of the acids prepared are summarized in Table I.

Experimental*

Preparation of the starting materials 4-Alkoxy-3,5-dimethoxybenzoic acids

Method "A" A mixture of methyl or *n*-butyl 4-hydroxy-3,5-dimethoxybenzoate (0.25 mole), acetophenone (180 ml), and pulverized anhydrous potassium carbonate (0.32 mole) was stirred for 5 minutes at 130—135°; the alkylating agent (0.32 mole) was added by drops

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* All melting points are uncorrected.

during 2 hrs., and the mixture stirred 7 to 30 hrs. at 135—145°. In one case boiling butanone was used as the solvent.

After cooling and filtration, the solvent was removed by distillation under reduced pressure or with steam, the residue dissolved in ether (200 ml), the ethereal phase extracted with 2% sodium hydroxide solution (300 ml), and the ether evaporated. The crude ester was hydrolyzed by boiling for 2 hrs. with 44% aqueous potassium hydroxide solution (33 ml) in methanol (400 ml). The methanol was distilled under reduced pressure, the residue dissolved in water (300 ml), extracted with ether (100 ml) and acidified with hydrochloric acid. After cooling the crude acid was filtered off, washed with water, dried in vacuum and recrystallized.

Method "B" *n*-Butyl 4-hydroxy-3,5-dimethoxybenzoate (0.25 mole) was mixed with a solution of sodium *n*-butoxide (0.3 mole) in *n*-butanol (300 ml); the alkylating agent (0.325 mole) was added by drops during 2 hrs. under stirring and boiling, and the mixture refluxed for 4 to 45 hrs. After cooling and filtration the butanol was removed in vacuum and the residue taken up in mixture of ether (200 ml) and water (200 ml). The ethereal phase was worked up in the same manner as in Method "A".

In the preparation of 4-allyloxy-3,5-dimethoxybenzoic acid, sodium methoxide was used in boiling methanol as the solvent.

2-Alkoxy-3,4-dimethoxybenzoic acids

Method "A" was employed, but the starting material was methyl 2-hydroxy-3,4-dimethoxybenzoate.

4-(2'-Dimethylaminoethoxy)-3,5-dimethoxybenzoic acid hydrochloride

A solution of 2-dimethylaminoethyl chloride (25.8 g) in dry benzene (200 ml) was added by drops to a vigorously stirred, boiling mixture of the sodium salt of methyl 4-hydroxy-3,5-dimethoxybenzoate (40.85 g) and methanol (175 ml); the mixture was boiled for 1 hr. more. After cooling, water (200 ml) and benzene (200 ml) were added, the benzene layer was extracted with 4% sodium hydroxide solution (200 ml) and dried over anhydrous potassium carbonate. After filtration the benzene was distilled in vacuum, the residue dissolved in anhydrous ether and acidified with 20% ethanolic hydrogen chloride (30 ml) to give 24.18 g of methyl 4-(2'-dimethylaminoethoxy)-3,5-dimethoxybenzoate hydrochloride, m. p. 191—193° (after recrystallization from a 1 : 1 mixture of acetone and ethanol).

$C_{14}H_{22}ClNO_5$ (320.4). Calcd. Cl 11.06; N 4.37. Found Cl 10.97; N 4.27%.

This ester (18.05 g) was hydrolyzed by boiling 2 hrs. with conc. hydrochloric acid (53 ml) in water (105 ml). After evaporation in vacuum, the residue was triturated with acetone, filtered off and dried to give 14.35 g of hydrochloride of the acid, decomposition point 249—251°.

$C_{13}H_{20}ClNO_5$ (306.4). Calcd. Cl 11.57; N 4.57. Found Cl 11.63; N 4.50%.

Acid chlorides

A mixture of the acid (0.05 mole), dry benzene (15 ml) and thionyl chloride (15 ml) was refluxed until the gas evolution ceased (in general, 1.5 hrs.); the solvent and excess thionyl chloride were then removed in vacuum. The crude acid chloride left behind were usually oils and used for the preparation of esters without further purification. Three of the acid chlorides, however, were crystalline: 4-*n*-propoxy-3,5-dimethoxybenzoyl chloride, m. p. 32—33° (from petroleum ether); 4-allyloxy-3,5-dimethoxybenzoyl chloride, m. p. 61—62° (from petroleum ether); and 4-(2'-dimethylaminoethoxy)-3,5-dimethoxybenzoyl chloride hydrochloride, m. p. 200—201° (after trituration with acetone).

N-(2'-hydroxyethyl)-2-methylmorpholine

Ethylene chlorohydrin (11.7 g) was added by drops during 1 hr. to 2-methylmorpholine (30 g) at 130° under stirring and the mixture was heated for another 1 hr. at the same temperature. After cooling, dry ether (250 ml) was added, the precipitate filtered off, the ether evaporated from the filtrate and the residue distilled in vacuum to give 14.72 g of the base, b.p. 94° at 7 mm or 100° at 10 mm.

$C_7H_{15}NO_2$ (145.3). Calcd. C 58.00; H 10.34; N 9.64. Found C 58.08; H 10.49; N 9.57%.

Preparation of the basic esters

Method "C". A solution of the basic alcohol (0.05 mole) in dry chloroform (10 ml) was added by drops to the acid chloride (0.05 mole) in dry chloroform (70 ml), with stirring and ice-cooling; the solution was then boiled for 8 hrs. and the solvent removed in vacuum. The residue was dissolved in water (200 ml), extracted with ether and the ethereal layer discarded. The aqueous solution was made alkaline with potassium hydrogen carbonate, the oily base extracted with ether (250 ml) and the ethereal layer dried over anhydrous potassium carbonate. After filtration a concentrated solution of the appropriate acid (0.06 mole) in ethanol was added, the precipitated salt filtrated off after cooling, and recrystallized.

Method "D". A mixture of the acid (0.02 mole), sodium isopropoxide (0.02 mole), isopropanol (50 ml) and diethylaminoethyl chloride hydrochloride (0.02 mole) was boiled for 12 hrs. and the hot solution filtered. The filtrate was evaporated in vacuum and the residue recrystallized.

The authors are indebted to the Analytical Department of the *Research Institute for Pharmaceutical Chemistry* for the analyses; to O. WINTERSTEIN for the preparation of materials; and to Mrs. I. FÜZESI and É. MOHAROS for their useful technical assistance.

SUMMARY

In order to examine the spasmolytic action, 28 basic esters of the title acids have been synthesized. Pharmacological evaluation revealed several relationships between the spasmolytic effect and the chemical structures of the acid and alcohol parts of the basic esters. The title acids have been prepared by alkylating the esters of 4-hydroxy-3,5-dimethoxy- and 2-hydroxy-3,4-dimethoxybenzoic acids, respectively.

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OPTICAL ROTATORY DISPERSION OF SOME MORPHINE AND CODEINE DERIVATIVES

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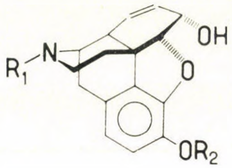
The study of the relations between optical rotation and the chemical structure and absolute configuration of organic compounds is one of the most important problems of stereochemistry [1]. Such studies have also included a number of nitrogen compounds, mainly primary amines and their derivatives [2, 3]. **Potapov** and **Terentiev** have recently subjected to a very detailed investigation the relationship between optical rotation and the absolute configuration of amines of the type $HR_1R_2CNH_2$ and their derivatives [3]. However in the nitrogen compounds investigated so far not the nitrogen atom, but the carbon structure is asymmetric, as there have been known but very few quaternary ammonium salts with definite absolute configuration. While the absolute configurations of a number of carbon compounds have been elucidated for some time, the first quaternary ammonium salt with known configuration was prepared not more than ten years ago [4]. However, all N-carboxymethyl-$3\alpha,6\beta$-dihydroxynortropane derivatives, as well as the later described morphine derivatives with known configurations contain besides the asymmetric quaternary nitrogen atom also asymmetric carbon atoms.

There is a considerable difference in the optical rotations of the N-stereoisomeric quaternary ammonium salts of morphine skeleton prepared earlier in this laboratory [5]. It seemed reasonable to study these rotation values in a wider range, and to compare them with that of other morphine derivatives. Our aim was to obtain from the rotatory dispersion studies — by taking into consideration some literature data — information on the rotatory power of the asymmetric nitrogen atom in morphine derivatives and on the configuration of these stereoisomeric quaternary salts.

As testified by recent literature, rotatory dispersion studies find increasingly wider use in the elucidation of the structural properties of optically active compounds [6]. Morphine derivatives have been studied by **Bobbitt** *et al.* [7] who found an anomalous dispersion curve around 300 mμ, but their studies did not include quaternary nitrogen compounds.

Emde [8] determined the direction of the rotation of the asymmetry centres $C_{(5)}$, $C_{(6)}$, $C_{(13)}$ and $C_{(14)}$ of the morphine skeleton by applying the principle of the optical superposition. In the present work we wish to report on our studies concerning the effect on the rotation of the substituents of the nitrogen atom in position 17 which is directly linked to the asymmetric carbon atoms $C_{(6)}$, $C_{(5)}$, $C_{(13)}$, $C_{(14)}$, $C_{(9)}$ in the morphine skeleton. This effect was investigated in the case of some bases, tertiary salts and of N-stereoisomeric quaternary salts.

Besides the N-stereoisomeric quaternary salt pairs with morphine skeleton prepared in this laboratory, BOGNÁR and SZABÓ [9] reported stereoiso-



I

	R_1	R_2
a	CH_3-	H
b	CH_3-	CH_3-
c	H	H
d	H	CH_3-
e	$CH_2=CH-CH_2-$	H

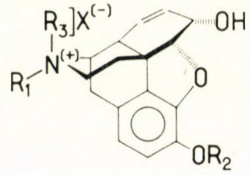
Fig. 1

meric $O_{(3)}$,$O_{(6)}$-diacetylmorphine quaternary salts. In the case of the latter compounds the direction of the optical rotations of the quaternary derivatives, obtained depending on the sequence of introducing the substituents of the nitrogen atom changes in the same way as found by us for morphine and codeine derivatives.

The rotatory power of $O_{(3)}$,$O_{(6)}$-diacetylmorphine-N-allyl bromide is $[\alpha]_D^{23} = -112.6°$ and that of $O_{(3)}$,$O_{(6)}$-diacetyl-N-allylnormorphine methobromide $[\alpha]_D^{23} = -152.9°$. It is a remarkable fact that the difference between the rotations of $O_{(3)}$,$O_{(6)}$-diacetylmorphine-N-*n*-propyl bromide and of $O_{(3)}$,$O_{(6)}$-diacetyl-N-*n*-propylnormorphine methobromide is practically the same as between the rotatory values of the former two compounds, namely 40.2°. BOGNÁR and SZABÓ, therefore, concluded that the contribution of the ring nitrogen atom to the asymmetry of the molecule is 20.1°—20.2°.

Discussion

The compounds with morphine structures which have been investigated by us are shown in Figs. 1 and 2. When the molecular rotation is plotted against the wavelength in the range studied, a smooth negative curve is obtained up to 295 mμ for all compounds, to be followed by the region of anomalous dispersion. At lower wavelengths the monotonous curves would probably show the negative Cotton effect which had been observed by **Bobbitt** *et al.*[7].

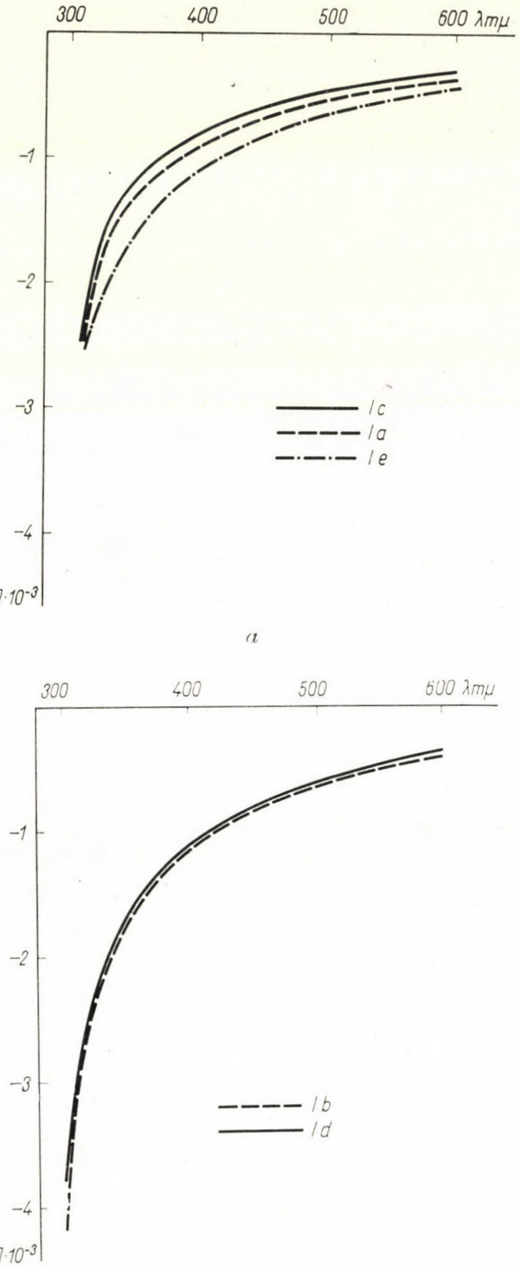


II

	R_1	R_2	R_3	$X^{(-)}$
a	H	CH_3-	H	$Cl^{(-)}$
b	H	CH_3-	H	$I^{(-)}$
c	CH_3-	CH_3-	H	$Cl^{(-)}$
d	CH_3-	H	H	$I^{(-)}$
e	$CH_2=CH-CH_2-$	H	H	$I^{(-)}$
f	CH_3-	H	$CH_2=CH-CH_2-$	$I^{(-)}$
g	$CH_2=CH-CH_2-$	H	CH_3-	$I^{(-)}$
h	CH_3-	CH_3-	$C_6H_5-CH_2-$	$I^{(-)}$
i	$C_6H_5-CH_2-$	CH_3-	CH_3-	$I^{(-)}$

Fig. 2

In accordance with the theory of rotatory dispersion, there is generally a considerable change in the molecular rotation towards the region of lower wavelengths, and the difference between the rotations of the corresponding compounds is also greater. Thus rotations measured at lower wavelengths may better used to establish the differences between compounds [10], in some cases, however, a comparison of the profiles of the curves over a wider range may also be of interest.


300
400
500
600 λmμ
−1
−2
−3
−4
[Φ]·10⁻³
I c
I a
I e
300
400
500
600 λmμ
−1
−2
−3
−4
[Φ]·10⁻³
I b
I d

a

b

Fig. 3

The λ values obtained by the one-term Drude equation [11] are lower (between 210 and 250 mμ) than the experimentally measured lower values (295—300 mμ). For this reason molecular rotations measured at 310 mμ (Φ_{310}) were used for comparison.

Substitution in position 3 of the skeleton brings about an unequivocal change extending over the entire spectrum range, as shown by the rotation values of morphine (**Ia**) and codeine (**Ib**) (Figs. 3a and 3b). In the case of norcodeine hydrohalides (**IIa** and **IIb**) the halide ions which compensate the positive charge of the nitrogen have also significant effect on the molecular rotation, in spite of the fact that in this case the nitrogen is no longer a centre of asymmetry. In the spectrum range investigated, norcodeine. HI (**IIb**) is more markedly laevorotatory than norcodeine. HCl (**IIa**) (Fig. 4).

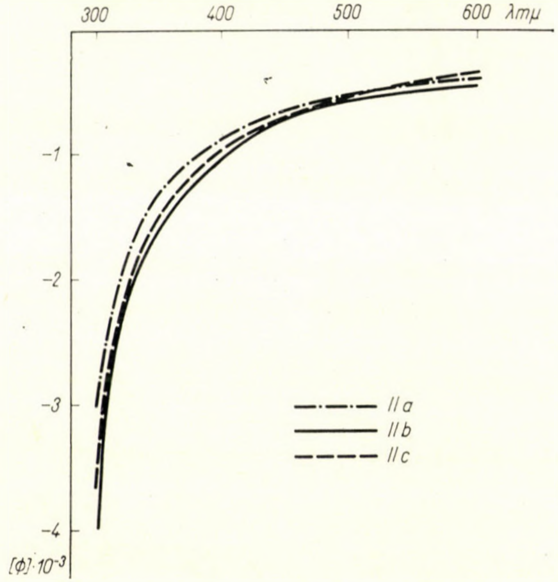


Fig. 4

Comparison of the rotations of normorphine (**Ic**) and morphine (**Ia**), further of norcodeine (**Id**) and codeine (**Ib**) shows that in the entire spectrum range the rotation values of the nor-compounds are lower (Figs. 3a and 3b), but at 600 mμ the rotation of norcodeine. HCl (**IIa**) is higher that of codeine. HCl (**IIc**). At 530 mμ the molecular rotation values of the two compounds are the same, and from this wavelength upwards the negative rotation of codeine. HCl (**IIc**) increases considerably more rapidly (Fig. 4).

N-Allylnormorphine.HI (**IIe**) has a higher negative rotation than morphine.HI (**IId**) (Fig. 5). The same is true for the corresponding bases (**Ia** and **Ie**)

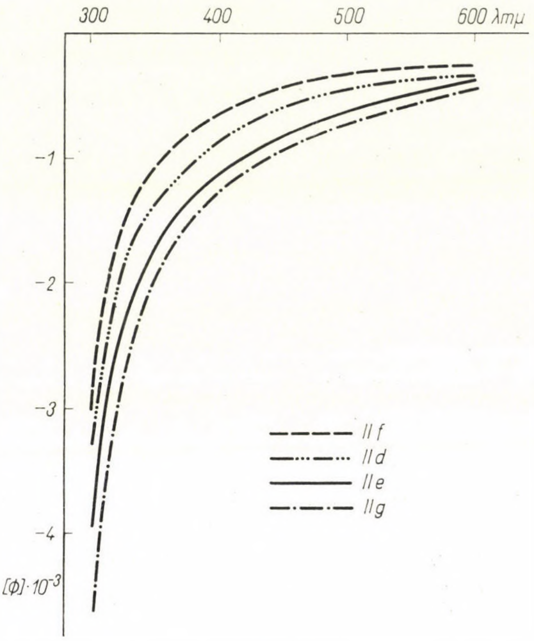

300
400
500
600 λmμ
−1
−2
−3
−4
[Φ]·10⁻³
II f
II d
II e
II g

Fig. 5

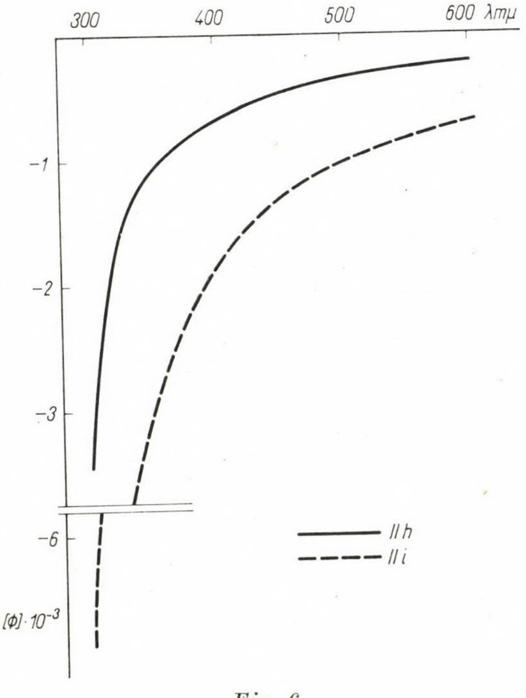

300
400
500
600 λmμ
−1
−2
−3
−6
[Φ]·10⁻³
II h
II i

Fig. 6

up to 325 mμ. Thus the compound which contains a larger and more polar group in equatorial position has also a higher molecular rotation.

Table I shows the molecular rotations, measured under identical conditions of the pairs morphine.HCl and morphine methochloride; morphine.HI and morphine methiodide; morphine 6-ethyl ether.HI and morphine 6-ethyl ether methiodide; codeine.HI and codeine methiodide.

It is seen from the table that in the case of all five pairs of salts the corresponding methocompound in which the nitrogen is no longer asymmetric has lower negative rotation.

By taking into consideration the aforesaid, it is reasonable to draw a comparison between the Φ values of N-stereoisomeric quaternary morphine derivatives. A comparison of the Φ value of morphine-N-allyl iodide (**IIf**) with that of N-allylnormorphine methiodide (**IIg**) shows that the values of the first compound are considerably lower over the entire spectral range (Fig. 5). The rotation of morphine-N-allyl iodide is also lower than that of N-allylnormorphine.HI (**IIe**) and even than that of morphine.HI (**IId**), while the Φ value of N-allylnormorphine methiodide, which is stereoisomeric on the nitrogen atom, is considerably higher than the values of the two former compounds.

Comparison of the Φ values of codeine-N-benzyl iodide (**IIh**) and N-benzylnorcodeine methiodide (**IIi**) (Fig. 6) shows an even more marked difference in the same direction between the members of the stereoisomeric salt pair.

Table I

Compound	M_D,	Note
Morphine. HCl	$-381°$	*a*
Morphine methochloride	$-349°$	*b*
Morphine. HI	$-349.2°$	*c*
Morphine methiodide	$-324.5°$	*d*
Morphine 6-ethyl ether. HI	$-551.3°$	*e*
Morphine 6-ethyl ether methiodide	$-476.9°$	*e*
Codeine. HCl	$-410.7°$	*f*
Codeine methochloride	$-221.4°$	*f*
Codeine. HI	$-400°$	*f*
Codeine methiodide	$-362°$	*g*

Note: *a* Own measurement water, 23°C, $c = 1$. Lit. [12] value: $-373.5°$ (water, 15°C, $c = 1$)
b Water, 29°C [13]
c Own measurement (water, 24°C) [15]
d Water, 25°C [14]
e Water, 24°C [15]
f Water, 27°C [13a]
g Own measurement (water, 25°C, $c = 1$)

In the range of lower wavelengths the deviation of the curves is more pronounced.

From all that has been said so far, the conclusion may be drawn that the difference between the rotation values of N-stereoisomeric quaternary salts increases parallel to the difference in the polarizability of the substituents attached to the nitrogen atom. It is also seen that the larger and more polar substituents in a stereoisomeric morphine or codeine quaternary salt increase the negative rotation when present in equatorial position, and they reduce when in axial position. The work of Bognár and Szabó also confirms that the polarity of the radical is not the only decisive factor. The Φ value of codeine-N-benzyl iodide (**IIh**) is lower than that of norcodeine hydroiodide (**IIb**). A comparison of the rotation values of the nor-compounds, N-alkyl derivatives, N-dimethyl compounds and of N-stereoisomeric quaternary salts afford unequivocal information about configuration of the latter compounds. It may be stated that the tertiary N-alkyl derivatives are more strongly laevorotatory than the corresponding nor-compounds, or the N-dimethyl derivatives.

Experimental

For the measurements a *Pepol 60* type photoelectric spectropolarimeter *(Bellingham and Stanley Ltd*, London) was used. The light source was a 250 watt XE/D/AEI compact xenon lamp (*Lamp and Lighting Co. Ltd.*, Leicester). The accuracy of the readings was, in the spectrum range investigated, higher than 0.003°. The measurements were made in a mixture of specially purified methanol and water (1:1 v/v), the thickness of the layer was 5 cm, and the temperature 23 ± 1°C.

Morphine (**Ia**) ($c = 0.2030$) $\Phi_{600} = -364°$, $\Phi_{589} = -382°$, $\Phi_{310} = -2570°$.

Codeine (**Ib**) ($c = 0.2026$) $\Phi_{600} = -402°$, $\Phi_{589} = -437°$, $\Phi_{310} = -3290°$, $\Phi_{300} = -4180°$.

Normorphine (**Ic**) ($c = 0.2008$) $\Phi_{600} = -292°$, $\Phi_{589} = -308°$, $\Phi_{310} = -2420°$, $\Phi_{300} = -2710°$.

Norcodeine (**Id**) ($c = 0.2013$) $\Phi_{600} = -370°$, $\Phi_{589} = -405°$, $\Phi_{310} = -2560°$, $\Phi_{300} = -3780°$.

N-Allylnormorphine (**Ie**) ($c = 0.2016$) $\Phi_{600} = -420°$, $\Phi_{589} = -421°$, $\Phi_{310} = -2480°$.

Norcodeine.HCl (**IIa**) ($c = 0.1992$) $\Phi_{600} = -326°$, $\Phi_{589} = -339°$, $\Phi_{310} = -2130°$, $\Phi_{300} = -3000°$.

Norcodeine.HI (**IIb**) ($c = 0.1984$) $\Phi_{600} = -399°$, $\Phi_{589} = -400°$, $\Phi_{310} = -3020°$, $\Phi_{300} = -3980°$.

Morphine.HI (**IId**) ($c = 0.2010$) $\Phi_{600} = -332°$, $\Phi_{589} = -333°$, $\Phi_{310} = -2660°$, $\Phi_{300} = -3280°$.

N-Allylnormorphine.HI (**IIe**) ($c = 0.2070$) $\Phi_{600} = -370°$, $\Phi_{589} = -424°$, $\Phi_{310} = -3270°$, $\Phi_{300} = -3940°$.

Morphine-N-allyl iodide (**IIf**) ($c = 0.2032$) $\Phi_{600} = -237°$, $\Phi_{589} = -260°$, $\Phi_{310} = -2430°$, $\Phi_{300} = -3030°$.

N-Allylnormorphine methiodide (**IIg**) ($c = 0.2058$) $\Phi_{600} = -431°$, $\Phi_{589} = -488°$, $\Phi_{310} = -3910°$, $\Phi_{300} = -4610°$.

Codeine-N-benzyl iodide (**IIh**) ($c = 0.1723$) $\Phi_{600} = -216°$, $\Phi_{589} = -231°$, $\Phi_{310} = -2600°$, $\Phi_{300} = -3450°$.

N-Benzylnorcodeine methiodide (**IIi**) ($c = 0.1876$) $\Phi_{600} = -688°$, $\Phi_{589} = -670°$, $\Phi_{310} = -5370°$, $\Phi_{300} = -6900°$.

The authors wish to thank Prof. Kálmán KOVÁCS the Director of the Institute, for his interest in this work and for his valuable advice.

SUMMARY

The optical rotation and optical rotatory dispersion of some bases and salts and N-stereoisomeric quaternary salt pairs have been investigated. Morphine and codeine methohalides are less laevorotatory than the correspodning hydrohalides. In the studied N-stereoisomeric salt pairs with morphine skeleton, the compounds prepared from the N-methyl derivatives with alkyl halides which contain the bulkier alkyl group on the nitrogen atom in axial position, are less laevorotatory than the quaternary salts obtained as the main products from the reaction of N-alkyl-nor-compounds with methyl halides.

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РЕЗЮМЕ

Применение диэлектрометрии в химических промышленных анализах

Ш. Б. НАДЬ

Диэлектрические измерения, проведённые на «заводском диэлектрометре», в промышленной измерительной ячейке с гофрированной трубкой, играют значительную роль, с точки зрения быстроты и простоты их проведения, а также их надёжности, при контроле процессов химической промышленности. Например, в случае исследования смесей уксусный ангидрид — уксусная кислота, толуол-хлористый бензол, и т. п. Для устранения мешающего действия температурной зависимости ДК, наилучшим оказался анализ, проводимый путём гармонического отбора проб и компенсирования температурной зависимости прибором, т. е. двумя осцилляторным диэлектрометром. Метод с применением «аполярного растворителя» наилучшим образом оправдал себя при последовательном наблюдении за реакцией сульфатирования спиртов жирного ряда и для индикации конечной точки реакции путём измерения «сопротивления потерь».

Определение железа с помощью радиометрического титрования, основанного на образовании комплекса

Й. КОНЕЦНИ, Й. ТЁЛДЕШИ и Т. БРАУН

Рассматривается радиометрическое титрование железа, основанное на образовании комплекса. В качестве измерительного раствора использовался 5.10^{-3} M раствор EDTA для разделения компонентов использовался катионообменник Dowex 50 W—X2, в качестве же индикатора — радионуклид $^{55+59}$Fe. Описывается сущность метода, ход работы и достигнутые результаты. С этим методом было определено количество железа в фармацевтических изделиях (**Tinctura Ferri aromatica**). Метод также используется для определения субмикрограммных количеств железа.

Изучение термического распада карбоната марганца II

А. Я. ХЕГЕДЮШ и А. Б. КИШ

При термическом распаде карбоната марганца (II), как и вообще в случае реакций термического распада, более точные информации о механизме реакции можно получить, если образующиеся в термовесах газообразные продукты распада переводить, с помощью какого-нибудь газа-носителя, в газовую кюветту ИК-спектрофотометра и регистрировать изменение абсорбции в зависимости от времени и температуры, путем регистрации абсорбционных максимумов ожидаемых газов, отдельно каждый при соответствующей длине волны.

Теория перехода фаз кристалл-жидкость

Ю. П. БАЗАРОВ

Последовательная статистическая теория плавления развивается в приближении самосогласующихся полей; это основывается на равенстве химических потенциалов кристаллической и жидкой фаз, сосуществующих одновременно. Найденные температуры плавления инертных газов соответствуют экспериментальным данным. Было выведено «правило половины», т. е. температура плавления (относительно давления атмосферы) равняется половине критической температуры для всех веществ с критическим давлением ниже 50 атмосфер.

О механизме адсорбции паров

Дь. СЕКЕЙ

Измерялось количество двуокиси углерода, связанное, образующимися после предварительного покрытия поверхности силикагельных проб ацетоном, системами силикагель — ацетон в зависимости от количества ацетона, внесенного на пробы. На основании полученных данных было установлено, что на крупнопористых пробах адсорбента, несмотря на покрытие большим количеством ацетона, имеются свободные части поверхности, на которых проходит связывание двуокиси углерода. На мелкопористом силикагеле количество таких свободных поверхностей очень мало уже в самом начале изотермы ацетона и эти поверхности быстро исчезают с увеличением степени покрытия ацетоном.

Некоторые новые проблемы механизма обмена веществ водорода и реакций гидрогенизации на металлических катализаторах, I. Каталитическая реакция обмена между метаном и тритием на Ni-катализаторе

Л. ГУЦИ, и П. ТЕТЕНИ

Исследовался гетерогенный каталитический обмен изотопов между CH_4 и HT, на никелевом катализаторе. Изучалась кинетика реакции и рассчитывалась величина энергии активации.

Установлено, что каталитический обмен проходит легче между HT и H_2, чем между CH_4 и HT. Этот факт, в согласии с термодинамическими расчетами, объясняется большей адсорбционной способностью водорода.

Некоторые топологические свойства молекул с ковалентной связью

Ф. БИЛЛЕШ

Установлено, что молекула как геометрическая форма может быть считана графом. Различные величины и функции были определены надэтим графом. Удалось топологически разделить различные типы молекул: молекулы центрального строения, ценные молекулы, плоские кольцевые и пространственные циклические молекулы. Были введены понятия об атоме симметрии и линии симметрии. С помощью этих понятий структурная матрица молекулы в значительной мере упрощается. Структурная матрица симметрии пригодна для ввода молекулярной структуры в вычислительные машины.

Реакция эфиров 2-оксо-5,5-ди(этокси)- и 2-оксо-5,5-этилендиокси-циклогексан-карбоновой кислоты с бромом, N-бром-сукцинимидом и двуокисью селена. Новая реакция ароматизации

К. ЛЕМПЕРТ, К. ШИМОН-ОРМАИ и Р. МАРКОВИЧ-КОРНИШ

1,4-циклогександион (Ia), а также его исследованные производные, а именно эфиры 5,5-диэтокси- и 5,5-этилендиокси-2-оксо-циклогексан-карбоновой кислоты (IVb и IVc) под воздействием элементарного брома, N-бром-сукцинимида или двуокиси селена ароматизируются в гидрохинон, эфир 5-этокси-салициловой кислоты (VIIa) или в 1,2-бис-(3-этокси-карбонил-4-гидрокси-фенокси)-этан (IX).

Синтетические линейные полимеры, XXV

Приближенный метод расчета точек плавления полиэфиров, полиамидов и полиэтиленов, содержащих группу SO_2

И. ГЕЦИ

Для расчета точек плавления полиэфиров, полиамидов и полиэтиленов, содержащих группу SO_2, использовался, данный автором ранее [12], метод определения, путем расчета, точек плавления макромолекул. Рассчитанные точки плавления хорошо совпадают с измеренными экспериментально температурами плавления. Необходимые для расчетов инкременты «молярная обратная точка плавления», были определены на основе данных Хорна [14]. Сравнение этих и приведенных ранее [12] величин инкрементов показало, что на величину инкремента атомных групп, находящихся в повторяющихся звеньях, оказывает также влияние наличие остальных атомных групп.

Исследования в области фунгицидов типа дитиокарбамата, I. Получение N-цианалкил- и N-карбоксиалкил-дитиокарбаматов

ДЬ. МАТОЛЧИ и ДЬ. ЙОШЕПОВИЧ

Были получены натриевые соли N-метил-N-β-цианэтил- и N-метил-N-β-карбоксиэтил-дитиокарбаминовой кислоты, а также несколько их S-замещенных производных с целью получения новых производных, аналогичных по биологическому влиянию производным диметил-дитиокарбаминовой кислоты, используемых в сельском хозяйстве в качестве фунгицида, но обладающих всасывающейся (системической) способностью. Исходя из метиламинпропионитрила и сероуглерода была синтезирована натриевая соль N-метил-N-β-цианэтил-дитиокарбаминовой кислоты, S-замещенные производные которой были получены по аналогии синтезу подобных производных диметилдитиокарбоновой кислоты. Образование карбоксильного радикала проходило путем последующего гидролиза циановой группы.

Производные алкокси-бензойных кислот, III

Основные сложные эфиры 4-алкокси-3,5-диметокси- и 2-алкокси-3,4-диметокси-бензойных кислот, обладающих подобно папаверину болеутоляющим действием

Е. КАСТРЕЙНЕР, Л. ВАРГА и Й. БОРШИ

Синтезировались 28 основных сложных эфиров перечисленных в названии статьи кислот с целью изучения их болеутоляющего действия. На основе фармакологического исследования было найдено несколько зависимостей между химической структурой кислотного и спиртового участка основных сложных эфиров и их болеутоляющим действием. Кислоты были синтезированы алкилированием эфиров 4-гидрокси-3,5-диметокси- и 2-гидрокси-3,4-диметокси-бензойных кислот.

Ротационная дисперсия нескольких производных морфина и кодеина

Г. БЕРНАТ, Й. А. САБО, К. КОЦКА и П. ВИНКЛЕР

Исследовалась оптическая способность вращения, а также оптическая ротационная дисперсия нескольких оснований и солей, имеющих скелет морфина, а также нескольких пар четверичных солей, стереоизомерных по азоту. Метогалоиды морфина и кодеина являются менее левовращающими, чем соответствующие гидрогалоиды. В случае исследованных, стереоизомерных по азоту, солевых пар, соединения, полученные из N-метил-производных и алкил-галогенидов, содержащих на азоте больший алкильный радикал в осевом положении, являются менее левовращающими, чем полученные из N-алкил-нор-оединений и метил-галоидов, в качестве главного продукта, четверичные соли.

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POLAROGRAPHIC DETERMINATION OF RARE EARTH IONS IN SOLUTIONS CONTAINING AMMONIUM LACTATE

J. INCZÉDY and L. ERDEY

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Received August 31, 1966

In the course of an earlier investigation [1], a method has been developed for the photometric determination of rare earth ions using a complex replacement reaction of the type:

$$\mathrm{Cu-EDTA} + \mathrm{RE}^{3+} \rightleftharpoons \mathrm{RE-EDTA} + \mathrm{Cu}^{2+}$$

The amount of replaced copper ion approximately equivalent to the rare earth ions was measured by a photometric method. The determination could be carried out directly in the effluent after ion exchange chromatographic separation of the rare earth ions, in the presence of ammonium lactate and lactic acid of fairly high concentration [2].

Recently some experiments have been made to develop a polarographic method for the determination of trace amounts of rare earths in a buffer solution of ammonium lactate and lactic acid, using the same or similar complex replacement reactions.

The direct polarographic method may be used only for the determination of europium and ytterbium [3]. Since the other rare earth ions are reducible at considerably higher potentials, the direct method cannot be applied to all species.

The aim of the present work has been to develop a polarographic method for the continuous analysis of rare earth mixtures after chromatographic separation, permitting the use of an automatic apparatus using lactic acid-ammonium lactate buffer solution as eluent, and avoiding the usual previous neutron activation [4].

It has been shown that the complex replacement method can be applied to the polarographic determination of the individual rare earths using a reagent solution containing copper(II) ethylenediamine tetraacetate or zinc ethylenediamine tetraacetate complex. The pH range 9.0—9.2 was found most convenient.

Experimental

Apparatus

Polariter PO 4 polarograph *(Radiometer*, Denmark); Precision pH-Meter Type OP 205 *(Radelkisz*, Hungary).

Reagents

Lanthanum chloride, samarium chloride and erbium chloride stock solutions of about 0.02 *M* concentration: Weighed amounts of the standard samples of the metal oxides *(Farbwerke Piesteritz*, G. D. R.) were dissolved in conc. hydrochloric acid and after careful evaporation almost to dryness, the residue was taken up in water and diluted in a volumetric flask to the volume required. The solutions were standardized by chelatometric titration using *Eriochrome Black T* indicator.

Copper(II) sulphate stock solutions of 0.1 and 0.02 *M*.

Zinc sulphate stock solutions of 0.1 and 0.02 *M*.

Disodium ethylenediamine tetraacetate (EDTA) standard solutions of 0.1 and of 0.02 *M*.

Cu-EDTA complex reagent solution of 0.05 *M*: 10 ml of the 0.1 *M* copper(II) sulphate stock solution was titrated with 0.1 *M* EDTA standard solution after the addition of some $NH_4Cl—NH_4OH$ buffer of pH 10, in the presence of Murexide indicator. In order to prepare a solution containing the stoichiometric complex, the same volume of EDTA solution as before was added from a burette.

Zn-EDTA complex reagent solution of 0.05 *M* was prepared similarly. For the preliminary titration Xylenol Orange indicator was used.

Lactic acid—ammonium lactate buffer solution (pH 3.4), 1 *M*: For its preparation see [1].

Ammonium hydroxide of sp. gr. 0.91 (analytical grade). 0.5% gelatin solution.

Polarographic measurements

A simple polarographic cell of 15 ml was used. Mercury to serve as the anode was filled first in the cell, then 10 ml of 1 *M* ammonium lactate solution of the required pH was added from a pipette. The pH of the lactate solution was checked on a pH-meter previously. To the solution the suitable portions of metal ion or complex solutions were added as required. Finally two drops of gelatin solution were added, the dropping mercury electrode was inserted, the mixture deaerated by bubbling nitrogen gas, and polarographed.

Estimation of rare earth ions using Cu-EDTA complex reagent solution

The lactic acid—ammonium lactate buffer solution sample of 10 ml was adjusted to pH 9.2 by the addition of some conc. ammonium hydroxide (ca. 1.2 ml). To the treated solution 4 ml of 0.05 *M* Cu-EDTA complex solution, and 2 drops of 0.5% gelatin solution were added. After deaeration by nitrogen, the solution was polarographed from 0 Volt using a low speed (sensitivity: 2 μA per 250 mm). After this blank experiment, known portions of the same rare earth stock solution were added to the same mixture. After each addition the mixture was let to stand 15 minutes, the cell was shortly deaerated, and the solution polarographed. On basis of the obtained wave height values calibration graphs were made, as shown in Fig. 3. The curves were found linear and the same in all cases, whether a lanthanum, erbium, samarium (or even copper) stock solution was given successively.

Estimation of rare earth ions using a reagent solution containing Zn-EDTA complex

The pH of the ammonium lactate buffer solution of 10 ml was adjusted to 9.2 by the addition of conc. ammonium hydroxide. 4 ml of the Zn-EDTA reagent solution, and 2 drops of 0.5% gelatin solution were added, and the mixture was polarographed with the usual speed from —1.0 Volt, after deaeration with nitrogen. (Sensitivity: 20 μA/250 mm). To the same mixture known portions of the rare earth stock solution were given successively, and after waiting for 15 minutes, the solution was polarographed again. On the basis of the obtained wave height data diagrams were constructed. One of them is shown in Fig. 6.

Results and discussion

Preliminary experiments have been made to investigate the polarographic behaviour of copper(II) ion in ammonium lactate solutions of pH 3—10, in the presence of EDTA. While at lower pH values the single reduction wave of copper(II) appears with a half-wave potential of ca. —0.32 V (against mercury anode), at higher pH values two waves are present at —0.12 and —0.40 V, corresponding to the two-step reduction. By successive addition of EDTA solution, the height of the wave (or waves) can be suppressed, and in the stoichiometric point only a very small wave remains corresponding to a quantity of "free", non-chelated, but rather ammine-complexed copper(II) ions (Fig. 1). If to this mixture — containing the stoichiometric quantities of copper and EDTA — trace amounts of rare earth ions are added, an approximately stoichiometric replacement by the later ion, *i.e.* stoichiometric increase of the wave height is observed, but only at higher pH values. As the optimum pH range 9.0—9.2 has been found. In this pH range if stoichiometric Cu-EDTA complex of higher concentration ($\sim$0.02 *M*) is present, only the first step of the "free copper" wave can be obtained clearly on the polarogram, because of the shifted but closely adjacent high wave of complexed copper.

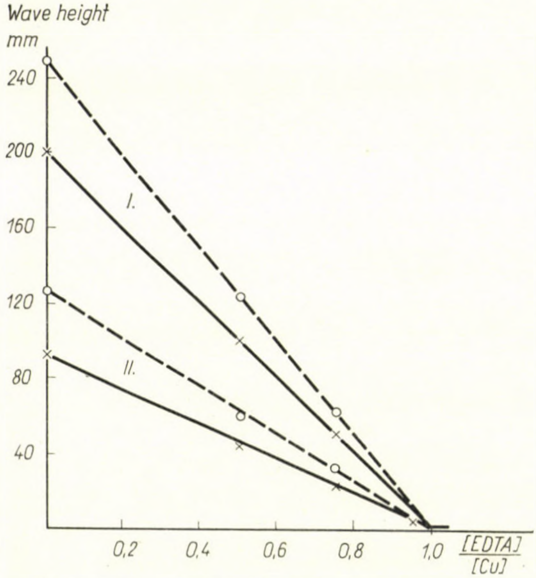

Fig. 1. Change of the polarographic wave heights of copper by successive additions of EDTA (Sensitivity.: 50 μA/250 mm)

- - - - - - in *M* $NH_4Cl—NH_4OH$ buffer solution of pH 9
——————— in 1 *M* NH_4-lactate solution of pH 9

To obtain a suitable polarogram it is necessary to apply slow measurement, *i.e.* a low speed should be used. The height of the remaning wave could not be diminished considerably by the addition of an excess of EDTA. To obtain a sensitive replacement effect, an excess of EDTA should be avoided, because such an excess would swallow the rare earth ions added, and so the results would be spoiled. Therefore, in later experiments a stoichiometric Cu-EDTA solution, prepared carefully previously, was always used. The Cu-EDTA reagent solution was added, to the ammonium lactate solution of pH 9.2 followed by the addition of a definite quantity of samarium or erbium or lanthanum [or also copper(II)] chloride stock solution. It was found that by increasing the metal ion content of the mixture, the height of the polarographic wave increased linearly up to 20 μmol. Above 5 μmol lower sensitivity (of 5 μA/250 mm) should be used. (See Figs 2 and 3).

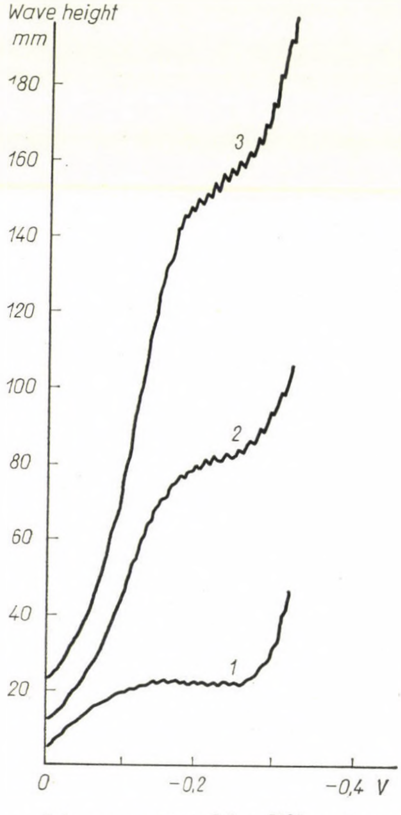

Fig. 2. Displacement polarographic waves caused by different quantities of lanthanum, using Cu-EDTA complex reagent in ammonium lactate solution of pH 9

1 in the absence of lanthanum, 2 in the presence of 1.75 μmol of La^{3+}, 3 in the presence of 3.5 μmol of La^{3+}

It was also found that for the total replacement some time was required. The higher the atomic number of the rare earth was, the slower the reaction took place. The rate of the replacement can be slightly increased by using the optimum pH range and a greater amount of Cu-EDTA complex. In the case of lanthanum about one minute, with samarium 10 minutes and with erbium 15—20 minutes were necessary to obtain complete replacement.

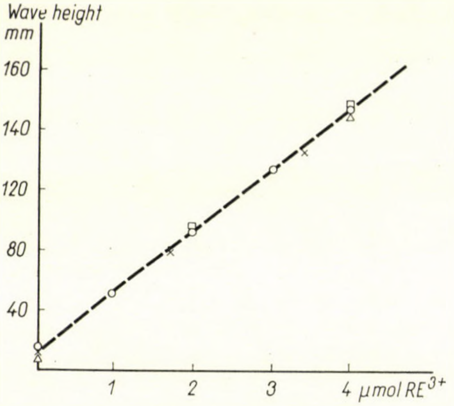

Fig. 3. Calibration curve for the estimation of rare earth ions using Cu-EDTA complex reagent (Sensitivity: 2 μA/250 mm)

□ Sm^{3+}, ○ Er^{3+}, × La^{3+}, △ Cu^{2+} ion

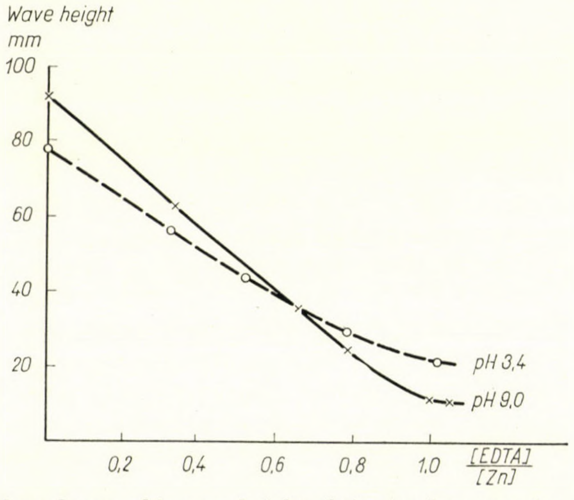

Fig. 4. Change of the polarographic wave height of zinc ion by successive additions of EDTA, in 1 M ammonium lactate solution (Sensitivity: 50 μA/250 mm)

Since the stability constant of the zinc-EDTA complex is lower than that of copper-EDTA, it was thought that more advantageous conditions might be attained by using zinc instead of copper. Polarographic measurements similar to those made with copper were carried out with zinc ions by the successive addition of EDTA standard solution in the presence of lactate buffer of

various pH as the base electrolyte. The height of the reduction wave (at about —1.2 V) of the "free" zinc ion was found to be decreased also to a rest value, as it can be seen in Fig. 4. However, the rest height was always much higher than that of copper, corresponding to the lower stability of the chelate complex formed with EDTA.

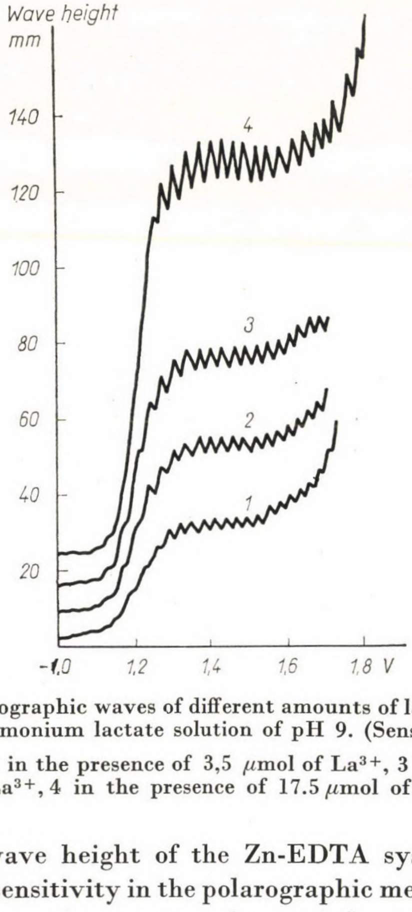

Fig. 5. Displacement polarographic waves of different amounts of lanthanum, using Zn-EDTA complex reagent in ammonium lactate solution of pH 9. (Sensitivity: 20 μA/250 mm)
1 in the absence of La^{3+}, 2 in the presence of 3,5 μmol of La^{3+}, 3 in the presence of 7,0 μmol of La^{3+}, 4 in the presence of 17.5 μmol of La^{3+}

Since the rest wave height of the Zn-EDTA system is much greater, one cannot use higher sensitivity in the polarographic measurements, and therefore the replacement experiments must be carried out with greater amounts of rare earths. In the range investigated, the increase of the wave height, caused by the replacement of various amounts of lanthanum, samarium, or erbium ion, was found to be in linear relation to the concentrations (Fig. 6). The optimum pH was found again at about 9. The time required to attain equilibrium was also similar to those of the experiments carried out with copper-EDTA complex.

It was also found that ammonium chloride—ammonium hydroxide buffer solution cannot be used instead of the NH_4OH—ammonium lactate solution.

In the investigated solutions containing copper (or zinc) ammonium and lactate (L^-) ions, ammonia and EDTA, the following complex formation reactions may be assumed:

$$Me^{2+} + \mathrm{EDTA} \overset{K_1}{\rightleftharpoons} Me\text{—}\mathrm{EDTA}$$

$$Me^{2+} + L^- \overset{K_{21}}{\rightleftharpoons} MeL^+$$

$$MeL^+ + L^- \overset{K_{22}}{\rightleftharpoons} MeL_2$$

$$Me^{2+} + \overset{NH_3}{\rightleftharpoons} \overset{K_{31}}{\rightleftharpoons} Me(NH_3)^{2+}$$

$$\cdot \qquad \cdot$$

$$\cdot \qquad \cdot$$

$$Me(NH_3)_3^{2+} + NH_3 \overset{K_{34}}{\rightleftharpoons} Me(NH_3)_4^{2+}$$

The stability constants of the copper complexes are: $\lg K_1 = 18.8$ [5]; $\lg K_{21} = 3.02$; $\lg K_{22} = 1.82$ [6]; and the successive stability constants of the ammine complex formation: $\lg K_{31} = 4.13$; $\lg K_{32} = 3.48$; $\lg K_{33} = 2.87$; and $\lg K_{34} = 2.11$ [7].

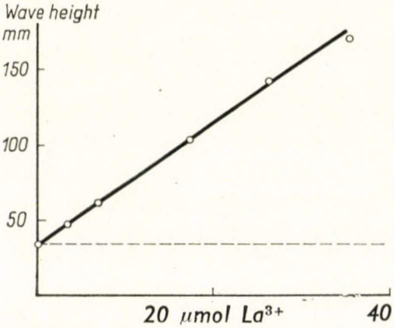

Fig. 6. Change of the wave height of the zinc ion by successive additions of increasing amounts of lanthanum ions (Sensitivity: 20 μA/250 mm)

The stability constants for zinc are the following; $\lg K_1 = 16.5$ [5]; $\lg K_{21} = 2.20$; $\lg K_{22} = 1.55$ [8]; $\lg K_{31} = 2.27$; $\lg K_{32} = 2.34$; $\lg K_{33} = 2.40$; and $\lg K_{34} = 2.05$ [7].

Considering the values of the stability constants and the concentration conditions in the solutions investigated, one can establish that in the solutions where copper or zinc are present, mainly the Me-EDTA complex will be produced, but also the ammine complex formation will be considerable at higher pH values. Much lower is the effect of the lactate ions in spite of the large quantity present. The probability of hydroxide complex formation is rather small. The main competing reactions are thus the EDTA and ammine complex formations.

The proneness of rare earth ions to form complexes with EDTA and with lactate ions are similar. But they do not form ammine complexes to any appreciable extent. The respective stability constants for lanthanum are the following; lg $K_1 = 15.5$ [5]; lg $K_{21} = 2.20$; lg $K_{22} = 1.80$; lg $K_{23} = 1.1$; for samarium: lg $K_1 = 17.14$ [5]; lg $K_{21} = 2.56$; lg $K_{22} = 2.02$; lg $K_{23} = 1.32$ [9]; and for erbium: lg $K_1 = 18.85$ [5]; lg $K_{21} = 2.77$; lg $K_{22} = 2.34$; lg $K_{23} = 1.59$ [9].

To obtain a complete replacement by the rare earth ions, the ammonia concentration has to be increased to such an extent, that the "conditional stability constant" of the copper-EDTA (or in the other case of the Zn-EDTA) complex becomes lower by at least two orders of magnitude than that of the respective rare earth complexes.

According to the experiments, the replacement is complete in solutions of pH 9—9.2. Considering the dissociation constant of ammonium hydroxide ($1.8 \cdot 10^{-5}$), and the approximately 1 *M* concentration of the ammonium ions in the solution, the concentration of the free ammonia ligand is about 0.5 *M*.

On basis of the concentrations and stability constants, the approximate conditional stability constants (K′) of the metal-EDTA complexes may be calculated from the following relation [10]:

$$\lg K_1' = \lg K_1 - \lg \alpha_1 - \lg (\alpha_2 + \alpha_3)$$

where α denotes the usual expressions:

$$\alpha_1 = 1 + [H] K_1^H + [H]^2 K_1^H K_2^H + \ldots$$

$$\alpha_2 = 1 + [L] K_{21} + [L]^2 K_{21} K_{22} + \ldots$$

$$\alpha_3 = 1 + [NH_3] K_{31} + [NH_3]^2 K_{31} K_{32} + \ldots$$

and K_i^H = the acidity constants of the EDTA.

The calculated approximate values are as follows:

$$\lg K_{1\,Cu}' = 18.8 - 1.4 - 11 = 6.4$$

$$\lg K_{1\,Zn}' = 16.5 - 1.4 - 8 = 7.1$$

$$\lg K_{1\,La}' = 15.5 - 1.4 - 5.1 = 9.0$$

$$\lg K_{1\,Sm}' = 17.14 - 1.4 - 5.9 = 9.84$$

$$\lg K_{1\,Er}' = 18.85 - 1.4 - 6.4 = 11.05$$

The calculated conditional constants are in agreement with the results of the experiments. In the used pH range the conditional constants of the rare earth complexes are greater by about three orders of magnitude than those of copper or zinc complexes.

The conditional constants of the Cu-EDTA and also that of the Zn-EDTA complex were calculated directly, using the concentration data obtained by the evaluation of the rest wave height of the metals in the solution containing stoichiometric amounts of metal ion and EDTA.

$$K'_{Cu} = \frac{[Cu-\mathrm{EDTA}]}{[Cu'][\mathrm{EDTA}']} = \frac{1.4\cdot 10^{-2}}{[7\cdot 10^{-5}]^2} = 2.9\cdot 10^6; \log K'_{Cu} = 6.46$$

$$K'_{Zn} - \frac{[Zn-\mathrm{EDTA}]}{[Zn'][\mathrm{EDTA}]} = \frac{1.4\cdot 10^{-2}}{(5\cdot 10^{-4})^2} = 5.6\cdot 10^4; \log K'_{Zn} = 4.75$$

The obtained log K'_{Cu} is very close to the calculated value. The deviation between the calculated and found values in the case of the zinc complex may be explained by kinetic effects occurring on the mercury electrode.

In our earlier investigation [1] where the replaced copper(II) ions were determined by photometry using Pyridylazo-2-naphtole indicator as the color reagent, it was not necessary to increase the ammonia concentration, since the copper(II)-EDTA complex was weakened not by ammine- but by PAN-complex formation.

The authors express their thanks to the Directorate of *VEB Stickstoffwerke, Piesteritz* (GDR) for the samples of rare earth oxides.

SUMMARY

The complex replacement polarography of some rare earth ions in ammonium lactate solutions has been investigated. Rare earth ions in ammoniacal solutions of pH 9 replace the complexed metal ions nearly stoichiometrically, if Cu-EDTA or Zn-EDTA complex is used as the reagent. By means of the polarographic measurement of the released copper (or zinc) ion, the rare earth ions may be estimated indirectly.

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DETERMINATION OF THE GAS CHROMATOGRAPHIC RETENTION INDICES OF VARIOUS ORGANOMETALLIC COMPOUNDS

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Since the discovery of gas chromatographic analytical procedures, numerous authors and committees have been dealing with the problem of expressing and collecting gas chromatographic retention data in a uniform way so as to make possible the general use of published results. Nevertheless, the problem has not been settled so far, and the lack of unambiguous expressions accepted and used by all authors is still evident. Recommendations based on a number of circumspective preliminary investigations have been elaborated by the Vth International Symposium of the *"Gas Chromatography Discussion Group"* (Brighton, September 1964) [1]. The unquestionable advantages of the proposed "retention index system", further the increasing popularity of this way of presentation of retention data in the last years clearly show that the outlines of a final solution of the problem have been laid down in the recommendations cited. This circumstance is one of the motives for writing this paper.

Gas chromatographic analyses of numerous organometallic compounds have been carried out in this laboratory during the last years in the course of various research programs. In order to facilitate our research work in the future, it has been regarded as useful to compile the most adequate and up-to-date data for the gas chromatographic characterization of those compounds which were available in a properly purified state.

The recommendations of the Vth International Symposium have not yet dealt with the standardisation of essential experimental conditions to be used in the course of the determination of retention indices. It is hoped, however, that the data obtained under the conditions chosen in the course of this work, may furnish information of general use as well.

General principles

The first proposal for the use of retention indices was elaborated by KOVÁTS in 1958 [2]. Recommendations of the Discussion Group were based on these proposals. In accordance with the recommendations, the following principles were kept in view.

Internal standards were used in the determination of the retention indices, I, of each compound. Normal alkanes served for this purpose and the measurements were carried out in the presence of at least two different normal alkanes. In all possible cases chromatograms were taken in the presence of three different n-alkanes, thus providing conditions for simultaneous determinations of the retention indices and the slope (b) of the graph of log retention volume against carbon number of the alkanes.

All retentions were corrected for the "dead volume" of the apparatus. The existence of the air-peak warranted the possibility for this correction when working with a thermo-conductivity cell (TC). In measurements performed with the aid of a flame ionization detector (FID), retention values were corrected by the retention of the methane peak.

Distances (mm) between the peak maxima of the air (or methane) peak and that of the investigated compounds were regarded as the characterizing data.

Calculation of the I values was based on the following formula:

$$I = 100\left(\frac{\log R_{XN}}{b} + N\right)$$

where

$$\log R_{XN} = \log R_X - \log R_N$$

and

$$b = \frac{\log R_{N+n} - \log R_N}{n}$$

R_X, R_N and R_{N+n} refer to retention values (mm) of the unknown compound and the n-alkanes containing N and $N + n$ carbon atoms, respectively.

Experimental

Measurements were carried out with the help of two *Fractovap Mod. C* apparatus (*CarloErba*, Milan). One of these was equipped with a Type-*P-AID/ff*, the other with a Type-*ATC/f* analytical unit. The *P-AID/ff* unit was provided with two FID-s which were operating independently in the course of this work, using two columns, two amplifiers and two recorder systems. A TC served as the detector in the *ATC/f* analytical unit. In this way, all determinations of the I values were accomplished on three different columns. I values of chlorosil anes were determined in an apparatus constructed in this laboratory. The TC of this device contained a glass-protected filament in order to avoid corrosion caused by hydrochloric acid. Experimental conditions are summarized in Table I.

Column packings (with the exception of that containing nitrotoluene) were dried and stabilized before the start of experiments at 200° in argon atmosphere for 24 hours at reduced pressure and the treatment at 200° was continued for several hours in carrier gas flow in the column as well. The carrier gas was dried over 5A molecular sieve, but no deoxygenization was employed.

Table I

Experimental conditions

Experimental parameter	Test substance		
	Chlorosilanes	Non-corrosive organic silicon compounds	
Detector	TC (glass protected)	TC	FID
Column dimensions	200 cm × 4 mm	200 cm × 4 mm	200 cm × 2 mm
Sample size	3—5 μl	1 μl	0.2 μl
Carrier gas	Hydrogen	Hydrogen	Nitrogen
Inlet pressure	1.5 kg/cm^2	1.5 kg/cm^2	2.0 kg/cm^2
Outlet pressure	Atmospheric in all experiments		
Carrier gas flow rates	50 ml/min	50 ml/min	20 ml/min
Support	*Chromosorb W*; treated with hexamethyldisilazane		
Mesh range of support	60—80 mesh in all experiments		
Origin of support	*Carlo Erba* (Milan)		
Stationary liquids (and their origin)	nitrotoluene *(Fluka AG)* *XF*-1112; nitrile-silicone fluid *(F & M)* *QF*-1; fluoro-silicone *(F & M)* *SE*-30 Silicone Gum Rubber *(Wilkens)*	Apiezon L (Edwards) *QF*-1; fluoro-silicone *(F & M)*	*SE*-30 Silicone Gum Rubber *(Wilkens)*
Weight per cent of stationary liquid	15	10	10

Retention measurements of a given substance were performed at a single temperature which was chosen in the region where width and symmetry of the chromatographic peak were found to be optimal. All determinations at the same temperature were carried out at the same adjustment of the thermostat and evaporator, in order to minimalize errors emerging from the adjustment of temperature. The accuracy of temperature control was ±0.05, ±0.1 and ±0.5 °C depending on the apparatus, the error of temperature adjustment did not exceed ±0.5 °C.

Purity of the internal standards was checked on conventional columns provided with an FID. Impurities occasionally found were not disturbing the accuracy of the determinations of either b or I values. b values, *i. e.* the slopes of the plot of log (retention volume) against carbon number for the normal alkanes, measured at different temperatures and on different columns are presented in Table II.

The results of retention index determinations are summarized in Tables III and IV. Table III lists the retention indices of chlorosilanes. The same data of various organosilicons and of some other organometallic compounds containing no hydrolyzable chlorine atoms are given in Table IV.

The origin and degree of purity of the samples listed in Tables III and IV were different. The total amount of impurities did not exceed 5% in the majority of cases. Compounds containing a higher per cent of impurities than the above-mentioned values are marked by an asterisk.

Table II

Temperature dependence of the slope of n-*alkane log plot*: b *on different columns*

Temperature, °C	30	40	60	80	100	120	140	160	180	200	220	240
APL		0.468	0.411	0.365	0.326	0.293	0.262	0.238	0.213	0.194	0.175	0.159
SE-30		0.409	0.362	0.320	0.286	0.255	0.227	0.202	0.182	0.166		
QF-1		0.354	0.312	0.272	0.238	0.218	0.187	0.170				
XF-1112		0.407	0.360									
Nitrotoluene	0.451	0.439										

Table III

Retention indices of chlorosilanes

No.	Nitrotoluene			*XF-1112* Nitrile silicone fluid			*QF-1* fluorosilicone			*SE-30* silicone gum rubber		
	Compound	Column temp. °C	*I*	Compound	Column temp. °C	*I*	Compound	Column temp. °C	*I*	Compound	Column temp. °C	*I*
1	$SiHCl_3$	30	561	$SiHCl_3$	40	520	$SiHCl_3$	40	549	$SiHCl_3$	40	491
2	$SiCl_4$	30	593	$MeSiHCl_2$	40	573	$SiCl_4$	40	609	$MeSiHCl_2$	40	508
3	$MeSiHCl_2$	30	620	$SiCl_4$	40	575	$MeSiHCl_2$	40	612	Me_3SiCl	40	553
4	Me_3SiCl	30	638	Me_3SiCl	40	607	Me_3SiCl	40	667	$SiCl_4$	40	569
5	$MeSiCl_3$	40	690	$MeSiCl_3$	40	650	$MeSiCl_3$	40	699	$MeSiCl_3$	40	598
6	Me_2SiCl_2	40	714	Me_2SiCl_2	40	666	$EtSiHCl_2$	40	718	Me_2SiCl_2	40	598
7	$CH_2{=}CHSiCl_3$	40	777	$EtSiHCl_2$	60	678	Me_2SiCl_2	40	725	$EtSiHCl_2$	40	620
8				$CH_2{=}CHSiCl_3$	60	735	$CH_2{=}CHSiCl_3$	40	768	$CH_2{=}CHSiCl_3$	40	685
9				$MeCH_2CHSiCl_2$	60	752	$MeCH_2{=}CHSiCl_2$	40	799	$EtSiCl_3$	40	703
10				$EtSiCl_3$	60	760	$EtSiCl_3$	40	803	Pr^iSiCl_3	60	778
11				Pr^iSiCl_3	60	828	Pr^iSiCl_3	60	884	Et_2SiCl_2	60	813
12				Et_2SiCl_2	60	886	Et_2SiCl_2	60	945			

Accuracy, reproducibility, possible sources of errors

Following the argumentation of ETTRE [3], an accuracy of presumably 0.5 units is needed in the measurement of I values (determined on three columns of different polarity), in order to characterize a particular compound unambiguously.

Peaks of organometallic compounds in a chromatogram may be selected with certainty with the aid of a method of this laboratory proposed in a previous paper [4]. The method is based on the detection of organometallic compounds with a mixed hydrogen-methane flame. Taking into account this possibility, the number of possible materials corresponding to I values within one index unit decreases considerably, so the assumed requirement of accuracy may be decreased in this case at least to 1—1.5 units.

Sources of possible random errors consist mainly in the inaccuracy of distance estimations and adjustment of temperature. These errors and those originating from inaccuracies of column temperature and carrier gas flow rate control (errors having the character of indeterminate errors) are by all means negligible compared to the following sources of systematic errors (determinate errors):

(1) Peak asymmetry as a consequence of too high amounts of sample introduced.
(2) Undefinite structure of the polymer used as the stationary phase and changes in its composition during use.
(3) Possibility of adsorption on the surface of the solid support material.
(4) Shifts in the position of peak maximum as a consequence of the presence of impurities resolved uncompletely from the main component of the test substance.

Our efforts to eliminate the effect of these factors are described in the experimental part of this paper.

In our opinion, the most important source of possible error lies in our case in the varying degrees of purity of the investigated samples. First of all, this type of error may lead to inaccuracies that vary from sample to sample. Furthermore, the magnitude of errors caused by this factor may be different even in the case of a definite substance when using different columns. In view of these, estimation of the accuracy of our I data is a rather difficult problem.

As for the reproducibility of our results, the data of parallel determinations were in agreement within 1 I unit in 92, 75 and 88% of all cases examined when working on columns containing *Apiezon L* (APL), *SE—30 Silicone Gum Rubber* or *QF—1 fluorosilicone*, respectively. The deviations from the average value in the remaining cases did not exceed ±1 I unit, either.

Discussion

It is evident from the data of Tables III and IV that systematic comparisons were possible only occasionally because of the eclectic nature of the collection of samples used throughout the experiments. Nevertheless, it was possible to draw some useful conclusions and to find out tendencies as well.

Connections between the retention index and molecular structure were investigated by KOVÁTS [5] in detail. It has been stated that ΔI values are of great importance in the identification of peaks or in the prediction of the retention indices of known compounds. (ΔI means the difference of I values determined on two stationary phases of different polarity, at the same temperature). ΔI values of various compounds were calculated from the data of Table III and are presented in Table V. The majority of data listed in Table V were based on I determinations performed at temperatures that were differing by 20 °C. ΔI values of this kind are presented in bracket in order to emphasize their approximative character. The following conclusions may be drawn from the ΔI and I data presented:

(1) A comparison of ΔSE—AP and ΔQF—SE* values has shown (and ΔI values not presented in Table V are no exceptions in this respect either) that both SE—30, which is apolar in its nature, and QF—1, which is more polar compared to SE—30, had a higher retarding effect on organometallic compounds than APL which consists purely of hydrocarbon compounds. As both SE—30 and QF—1 are polymers containing Si—O—Si skeleton, ΔSE—AP values are characterizing the degree of interaction between the siloxane skeleton and the different types of organometallic structures tested, while ΔQF—SE values depend mainly on the nature of the organic substituent of the organometallic compound in question.

(2) It is not surprising, therefore, that the numerical values of ΔSE—AP were found to be the highest in the case of dimethylsiloxanes. Further, it may be observed that these values are increasing as the number of $(CH_3)_2SiO$ units is higher. The increment amounts to 50—60 $\Delta I/(CH_3)_2SiO$ unit on the average.

(3) It is interesting, although easy to understand that compounds containing $\equiv$Si—O—C$\equiv$ bonds, *i. e.* compounds characterized by the general formula $R_nSi(OR')_{4-n}$ are next to the solute materials containing the siloxane skeleton as regards their retarding effect on siloxanes, when used as the stationary phases (solvents). ΔSE—AP values are increasing also in this case with the increasing number of OR′ groups, but the degree of variations is influenced naturally by the length of the R and R′ radicals. In all cases tested so far, ΔSE—AP values are lying between the limits of 50—85 in compounds of this type, despite manyfold variations of R, R′ and n.

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* The following abbreviations will be used throughout the text: ΔI (SE 30—APL) = = ΔSE—AP, and ΔI (QF—1-SE—30) = ΔQF—SE.

Table IV

Retention Indices of Organometallic Compounds

Stationary liquid		APL			SE—30			QF—1		
No 1.	No of C atoms	Compound	Temp., °C	I	Compound	Temp., °C	I	Compound	Temp., °C	I
1	4				$SiMe_4$	40	453			
2	4	$Si(OMe)_4$	60	686	$Si(OMe)_4$	60	766	$Si(OMe)_4$	60	913
3	5	$Me_3SiCH{=}CH_2$	40	522	$Me_3SiCH{=}CH_2$	40	551	$Me_3SiCH{=}CH_2$	40	563
4	5	Me_3SiEt x	40	547	Me_3SiEt x	40	573	Me_3SiEt x	40	581
5	5	$Me_3Si(OEt)$ x	60	612	$Me_3Si(OEt)$ x	60	687			
6	6	$(Me_3Si)_2O$	60	612	$Me_3SiCH_2CH{=}CH_2$	40	653	Me_3SiPr^i	40	668
7	6	$Me_3SiCH_2CH{=}CH_2$	60	625	Me_3SiPr^i	40	659	$(Me_3Si)_2O$	40	690
8	6	Me_3SiPr^i	40	637	$(Me_3Si)_2O$	60	687	$Me_3SiCH_2CH{=}CH_2$	40	690
9	6	$Me_2Si(OEt)_2$	60	703	$Me_2Si(OEt)_2$	60	758	$(Me_2SiO)_3$	60	810
10	6	$(Me_2SiO)_3$	80	723	$MeBu(OMe)SiH$ x	80	785	$Me_2Si(OEt)_2$	40	831
11	6	$MeBu(OMe)SiH$ x	80	755	$(Me_2SiO)_3$	80	818			
12	7	$Me_3SiCH_2CH_2CH{=}CH_2$	60	721	$Me_3SiCH_2CH_2CH{=}CH_2$	60	748	$Me_3SiCH_2CH_2CH{=}CH_2$	60	784
13	7	$(Me_3Si)_2CH_2$	80	778	$(Me_3Si)_2CH_2$	80	818	$(Me_3Si)_2CH_2$	60	849
14	7	$MeSi(OEt)_3$	80	800	$Me_2Si(CH_2)_4CH_2$	100	846	$Me_2Si(CH_2)_4CH_2$	60	865
15	7	$Me_2Si(CH_2)_4CH_2$	100	840	$MeSi(OEt)_3$	80	872	$MeSi(OEt)_3$	60	950
16	8	$Me_2Si(OPr^i)_2$ x	80	731	$Me_2Si(OPr^i)_2$ x	80	791	$Me_2Si(OPr^i)_2$ x	60	844
17	8	$Me_3Si(OSiMe_2)OSiMe_3$	100	758	$(CH_2{=}CHMe_2Si)_2O$	100	851	$(CH_2{=}CHMe_2Si)_2O$	60	856
18	8	$(CH_2{=}CHMe_2Si)_2O$	100	772	$Me_3Si(OSiMe_2)OSiMe_3$	100	879	$Me_3Si(OSiMe_2)OSiMe_3$	60	883
19	8	$(Me_2EtSi)_2O$	100	826	$(Me_2EtSi)_2O$	100	898	$(Me_2EtSi)_2O$	60	898
20	8	$(Me_2SiO)_4$	100	844	$Me_2Si(OPr^n)_2$ x	100	923	$(Me_2SiO)_4$	80	971
21	8	$Me_2Si(OPr^n)_2$ x	100	859	$Si(OEt)_4$	100	969	$Me_2Si(OPr^n)_2$ x	60	985
22	8	$Si(OEt)_4$	100	875	$(Me_2SiO)_4$	120	988	$Si(OEt)_4$	80	1043
23	8	Ge_3Me_8	120	1069	Ge_3Me_8	120	1144	Ge_3Me_8	100	1187
24	8	$(OEt)_3SiCHBrCH_2Br$	200	1392	$(OEt)_3SiCHBrCH_2Br$	180	1448	$(OEt)_3SiCHBrCH_2Br$	160	1668
25	9	$CH_2{=}CHCH_2Si(OEt)_3$	140	929	$MeBu_2SiH$	120	997	$MeBu_2SiH$	80	1013
26	9	$MeBu_2SiH$	120	975	Me_3SiPh	120	1004	$CH_2{=}CHCH_2Si(OEt)_3$	100	1077
27	9	Me_3SiPh	120	993	$CH_2{=}CHCH_2Si(OEt)_3$	140	1012	Me_3SiPh	80	1112
28	9	$Me_3Si(OPh)$	140	1022	$Me_3Si(OPh)$	140	1049	$Me_3Si(OPh)$	120	1207
29	9	$PhSi(OMe)_3$	140	1145	$PhSi(OMe)_3$	140	1201	$PhSi(OMe)_3$	140	1392
30	10	$Me_2Si(OBu^t)_2$ x	80	773	$Me_2Si(OBu^t)_2$ x	80	840	$Me_2Si(OBu^t)_2$ x	60	882
31	10	$Me_3Si(OSiMe_2)_2OSiMe_3$	140	880	$CF_3C_6H_4SiMe_3$	140	1004	$CH_2{=}CHMe_2Si(OSiMe_2)OSiMe_2CH{=}CH_2$	120	1017
32	10	$CH_2{=}CHMe_2Si(OSiMe_2)OSiMe_2CH{=}CH_2$	140	901	$Me_2Si(OBu^s)_2$	100	1019	$Me_3Si(OSiMe_2)_2OSiMe_3$	100	1052
33	10	$CF_3C_6H_4SiMe_3$	140	933	$CH_2{=}CHMe_2Si(OSiMe_2)OSiMe_2CH{=}CH_2$	140	1034	$Me_2Si(OBu^s)_2$	80	1053
34	10	$Me_2Si(OBu^s)_2$	100	947	$Me_3Si(OSiMe_2)_2OSiMe_3$	140	1064	$Me_2Si(OBu)_2$	100	1117
35	10	$(Me_2SiO)_5$	140	951	$(CH_2{=}CHCH_2)_2Si(OEt)_2$	140	1086	$(Me_2SiO)_5$	100	1142
36	10	$(CH_2{=}CHCH_2)_2Si(OEt)_2$	140	1015	$CH_2{=}CHMe_2SiPh$	120	1089	$(CH_2{=}CHCH_2)_2Si(OEt)_2$	100	1154
37	10	$CF_3C_6H_4SiMe(OMe)_2$	140	1024	Me_3SiCH_2Ph	120	1091	$CF_3C_6H_4SiMe_3$	120	1195
38	10	$Me_2Si(OBu)_2$	140	1030	$Me_2Si(OBu)_2$	120	1097	$CH_2{=}CHMe_2SiPh$	100	1196
39	10	Me_3SiCH_2Ph	120	1073	$Me_3SiC_6H_4Me$	120	1102	$Me_3SiC_6H_4Me$	100	1196
40	10	$CH_2{=}CHMe_2SiPh$	140	1087	$CF_3C_6H_4SiMe(OMe)_2$	140	1124	Me_3SiCH_2Ph	100	1223
41	10	$Me_3SiC_6H_4Me$	140	1100	$(Me_2SiO)_5$	140	1154	$CF_3C_6H_4SiMe(OMe)_2$	140	1346
42	10	Ge_4Me_{10}	180	1366	Ge_4Me_{10}	180	1473			
43	11	$CH_2{=}CHMe_2Si(OSiMeCH{=}CH_2)OSiCH{=}CH_2Me_2$	140	974	$CH_2{=}CHMe_2Si(OSiMeCH{=}CH_2)OSiCH{=}CH_2Me_2$	140	1113	$CH_2{=}CHMe_2Si(OSiMeCH{=}CH_2)OSiCH{=}CH_2Me_2$	120	1112
44	11	$(CH_2{=}CHCH_2)_3Si(OEt)$	140	1104	$(CH_2{=}CHCH_2)_3Si(OEt)$	140	1156	$(CH_2{=}CHCH_2)_3SiOEt)$	100	1240
45	11	$CH_2{=}CHCH_2Me_2SiPh$	160	1187	$CH_2{=}CHCH_2Me_2SiPh$	140	1191	$CH_2{=}CHCH_2Me_2SiPh$	140	1323
46	11	$MePhSi(OEt)_2$	180	1194	Me_2Pr^iSiPh x	160	1236	Me_2Pr^iSiPh x	140	1347
47	11	Me_2Pr^iSiPh x	180	1225	$MePhSi(OEt)_2$	160	1237	$MePhSi(OEt)_2$	140	1363
48	12	$(Me_2SiO)_6$	180	1073	$[(OEt)_3Si]_2O$	160	1315	$(Me_2SiO)_6$	140	1318
49	12	$[(OEt)_3Si]_2O$	140	1141	$(Et_3Si)_2O$	160	1331	$(Et_3Si)_2O$	140	1335
50	12	$PhSi(OEt)_3$	180	1263	$PhSi(OEt)_3$	160	1334	$[(OEt)_3Si]_2O$	140	1383
51	12	$(Et_3Si_2)O$	160	1267	$(Me_2SiO)_6$	160	1336	$PhSi(OEt)_3$	140	1475
52	12	$(SiMe_2)_6$	240	1675	$(SiMe_2)_6$	200	1743			
53	12	Ge_5Me_{12}	240	1712	Ge_5Me_{12}	200	1785			
54	14	$(Me_2SiO)_7$	180	1221	$(Me_2SiO)_7$	180	1514	$(Me_2SiO)_7$	140	1502
55	15	$(CH_3CHC_6H_3)SiMeH$			$(CH_3OHC_6H_3)_2SiMeH$	200	1777			
56	16	$(OEt)_3SiOSi(OEt)_2OSi(OEt)_3$	220	1376	$(OEt)_3SiOSi(OEt)_2OSi(OEt)_3$	180	1612	Bu_4Sn	140	1667
57	16	Bu_4Sn	220	1596	Bu_4Sn	180	1668	$(OEt)_3Si\ OSi(OEt)_2OSi(OEt)_3$	140	1707
58	16	$Ph_2Si(OEt)_2$	240	1671	$Ph_2Si(OEt)_2$	200	1702			
59	18	$(PhCH_2{=}CHMeSi)_2O$	240	1773	$(PhCH_2{=}CHMeSi)_2O$	200	1839			
60	20	$(OEt_3)Si[OSi(OEt)_2]_2OSi(OEt)_3$	220	1480	$(OEt)_3Si[OSi(OEt)_2]_2OSi(OEt)_3$	180	1607	$(OEt)_3Si[OSi(OEt)_2]_2OSi(OEt)_3$	140	1702

Table V

ΔI values of some organosilicon compounds

N°	Compound	Column temperature, °C			ΔSE-AP	ΔQF-SE
		APL	SE—30	QF—1		
27	Me_3SiPh	120	120	80	11	(108)
39	Me_3SiCH_2Ph	120	120	100	18	(131)
41	$Me_3SiC_6H_4Me$	140	120	100	(2)	(94)
40	$Me_2CH_2{=}CHSiPh$	140	120	100	(2)	(107)
45	$Me_2CH_2CH{=}CH_2SiPh$	160	140	140	(4)	132
47	Me_2Pr^iSiPh	180	160	140	(10)	(111)
4	Me_3SiEt	40	40	40	26	8
8	Me_3SiPr^i	40	40	40	22	9
3	$Me_3SiCH{=}CH_2$	40	40	—	29	—
7	$Me_3SiCH_2{=}CHCH_2$	60	60	40	29	(37)
12	$Me_3SiCH_2CH_2CH{=}CH_2$	60	60	60	27	36
2	$Si(OMe)_4$	60	60	60	80	147
44	$(CH_2{=}CHCH_2)_3SiOEt$	140	140	100	52	(85)
36	$(CH_2{=}CHCH_2)_2Si(OEt)_2$	140	140	100	71	(67)
25	$CH_2{=}CH_2Si(OEt)_3$	140	140	100	83	(65)
9	$Me_2Si(OEt)_2$	60	60	40	54	(74)
14	$MeSi(OEt)_3$	80	80—60	60	74	73
22	$Si(OEt)_4$	100	100	80	93	(74)
21	$Me_2Si(OPr^n)_2$	100	100	60	63	(63)
16	$Me_2Si(OPr^i)_2$	80	80	60	60	(53)
38	$Me_2Si(OBu^p)_2$	140	120	100	(67)	(20)
34	$Me_2Si(OBu^s)_2$	100	100	80	72	(35)
30	$Me_2Si(OBu^t)_2$	80	80	60	66	(43)
10	$(Me_2SiO)_3$	80	80—60	60	94	—13
20	$(Me_2SiO)_4$	100	100	80	150	(—23)
35	$(Me_2SiO)_5$	140	140	100	203	(—11)
48	$(Me_2SiO)_6$	180	160	140	(263)	(—17)
54	$(Me_2SiO)_7$	180	180	140	292	(—11)
6	$(Me_3Si)_2O$	60	60	40	75	(3)
17	$Me_3Si(OSiMe_2)OSiMe_3$	100	100	60	122	(4)
31	$Me_3Si(OSiMe_2)_2OSiMe_3$	140	140	100	184	(—12)

(4) The interval of ΔSE—AP values (2—30) found to be characteristic for organo-silanes having the general formula $R_nSiR'_{4-n}$, may well be distinguished from ΔSE—AP values of the compounds mentioned above. At the same

time, values (2—11) for organosilanes containing phenyl radicals significantly differ from those (22—29) which do not contain aromatic constituents.

(5) The above regularities may be concealed, of course, due to combined effects. *E. g.*, ΔSE—AP = 28 has been obtained in the case of Me_3SiOPh. On basis of this result an organosilane (without phenyl groups) could easily be suspected in a chromatogram consisting of unknown components. It is evident, however, that simultaneous effects of the Ph and $\equiv$Si—O—C$\equiv$ groups are reflected in this value. The possibility of errors of this type may be reduced to a considerable extent if not only ΔSE—AP but ΔQF—SE values are also available. (ΔQF—SE equals 158 in the case of Me_3SiOPh.)

(6) ΔQF—SE values are small positive, sometimes even negative numbers in the case of dimethylsiloxanes. Similarly, the differences in the retentions of *normal*- and *iso*-alkane substituted monosilanes are not considerable on QF—1 and SE—30, respectively. On the other hand, ΔQF—SE is increasing in a typical way when the substituent R is unsaturated. This result is in full agreement with data obtained with hydrocarbon compounds, and may be explained by the polarizing effect of the polar stationary phase on π electrons of the solute molecule [7].

(7) ΔQF—SE values are rather characteristic data for compounds belonging to the $R_nSi(OR')_{4-n}$ type although they vary within broad limits. Values presented in Table V point to the fact that the magnitude of these values is determined primarily by the length of the R′ substituent. The relative amount (n) of polar and apolar groups within the molecule, further the length of R seem to be additional factors in this respect.

(8) The presence of phenyl groups in the molecule is indicated by the highest values of ΔQF—SE. This fact together with the other circumstances already mentioned (namely extremely low ΔSE—AP values) allow the recognition of phenyl-substituted organic silicon compounds with great certainty.

(9) Although the relatively small number of experimental data does not alow the formulation of an unequivocal rule, a further and probably interesting connection may be guessed if *I* values of Ge_3Me_{10}, Ge_5Me_{12} and Si_6Me_{12} — presented in Table IV — are compared with *I* values of all other organometallic compounds containing corresponding numbers of carbon atoms. The former compounds are all showing comparatively high retention indices, corresponding to values estimated by summarizing the carbon and metall atoms in the molecule, similarly as retention indices of straight chain hydrocarbons may be estimated by summarizing the carbon atoms in the molecule. ($C + Ge = 11$; $I^{APL} = 1069$, $C + Ge = 14$; $I^{APL} = 1366$, $C + Ge = 17$; $I^{APL} = 1712$, $Si + C = 18$; $I^{Se-30} = 1743$).

This tendency is substantiated by an additional fact. Let us regard the ∂I values, *i.e.* the differences of *I* values of successive homologous dimethylsilanes and dimethylgermanes, measured on the same column and at the same temperature. If operating temperatures are similar, as in the case of Ge_4Me_{10} and Ge_5Me_{12} on SE—30, a ∂I value of approximately 300 may be derived for one $Ge(CH_3)_2$ unit. This equals the index-increment for three CH_2: groups, according to the statement of KOVÁTS. The increment for a $(CH_3)_2SiO$: unit amounts only to 160 and 120 I units on APL and QF—1, respectively (see Fig. 1 and discussion below).

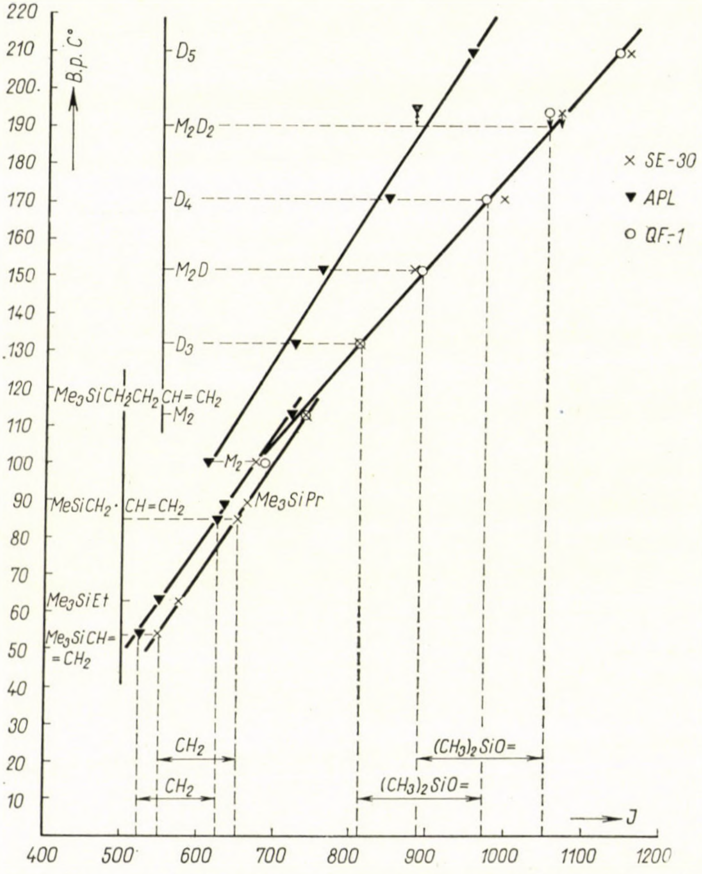

Fig. 1. Retention index *vs.* boiling point diagrams of dimethylsiloxanes and alkylsilanes

M_2: Hexamethyldisiloxane; D_3: hexamethylcyclotrisiloxane; M_2D: octamethyltrisiloxane; D_4: octamethylcyclotetrasiloxane; M_2D_2: decamethyltetrasiloxane; D_5: decamethylcyclopentasiloxane

(10) I values of organosilanes ($R_nSiR'_{4-n}$) and of methylpolysiloxanes [$(SiO)_n(CH_3)_{2n}$ and $(SiO)_n(CH_3)_{2n+2}$] are demonstrated in Fig. 1 as functions of the boiling points of the corresponding compounds. It is seen that all data measured on a particular column are found along a single straight line for both saturated and unsaturated silanes, while data for siloxanes are situated along another straight line, common for both linear and cyclic siloxanes. The linear

relation between I values and boiling points of silanes holds true only when APL or SE—30 are used as the stationary phase. Retention indices of siloxanes are almost equal both on QF—1 and SE—30, thus linear curves are obtained on all three columns. The slope in the case of APL is steeper than that of the common linear curves of SE—30 and QF—1.

As it is known [6], the linear connection of log V_g and the boiling point, consequently also of I and the boiling point is of an approximative character and is valid only with the following two restrictions:

(1) Enthalpy changes arising from blending of the components and the stationary liquid must be negligible, and

(2) entropy changes of the same process must be of the same magnitude with respect to each component.

According to the evidence of Fig. 1 these requirements are fulfilled in our case and the solutions of dimethylsiloxanes in all three stationary liquids may be considered to be close to ideal. Further, in spite of differences manifested in their chain or ring structure, the investigated dimethylsiloxanes seem to behave like homologous compounds.

The formation of nearly ideal solutions may also be observed between the mentioned organosilanes and the stationary phases APL and SE—30. On the other hand, the retention of unsaturated organosilanes on QF—1 is considerably higher than that of saturated ones. ΔQF—SE values of compounds containing double bonds have called attention to this fact already.

Let us consider now the boiling point *versus* I graphs of the siloxanes in Fig. 1.

A further evidence for the homologous behaviour of the siloxanes in question is furnished by the fact that their boiling points divide the Y axis of the diagram into sections of almost equal length, according to the well-known empirical relation:
$T_b = k_1 + k_2 \cdot n$ (n = number of homologous units). Small deviations may be observed for M_2D_2, and a considerable one for M_2 in this respect.

As a consequence of the homologous behaviour of cyclic and linear dimethylsiloxanes indicated in Fig. 1, we may conclude that the contribution of a SiO group to the retention index is of about the same magnitude as that of two methyl groups. That means:

$$\partial^{I}/(CH_3)_2SiO \cong 2(\partial^{I}/2\ CH_3) \cong 2(\partial^{I}/SiO) \cong 160$$

on SE—30 and QF—1,

while $\partial^{I}/(CH_3)_2SiO \cong 2(\partial^{I}/2\ CH_3) \cong 2\ (\partial^{I}/SiO) \cong 120$ on APL may be evaluated.

The two retention diagrams of compounds of the type $R_nSiR'_{4-n}$ show very impressively that the increment for a CH_2: unit equals 100 in this group of compounds, too [2].

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SUMMARY

Retention indices of 68 Si organic and of some Ge and Sn organic compounds were determined on columns that contained *Apiezon* L, *SE*—30 Silicone Gum Rubber, *QF*—1 fluorosilicone, *XF-1112* nitrile-silicone-fluid and *o*-nitrotoluene as stationary phases. All determinations were carried out according to the "Recommendations" of the *Gas Chromatography Discussion Group Data Sub-committee.*

Based on *a)* ΔI values calculated from retention indices determined on different columns, and *b)* retention index increments (∂I) for successive homologous compounds found when using a definite column, some rules and connections of generalisable character were established concerning the gas chromatographic behaviour of the investigated substances. This renders a possibility for the most suitable choice of columns in cases where the sample-composition is known, or for identification of peaks when the sample is an unknown one.

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DETERMINATION OF OPTIMUM SCHEDULE AND SENSITIVITY FOR NON-DESTRUCTIVE ACTIVATION ANALYSIS

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Introduction

In activation analysis the activation of elements other than those to be measured presents usually an inconvenient interference with the activity measurement. The effect of these interfering activities may be eliminated by chemical separation or half-life measurements, but in the case of serial analysis covering a large number of samples both techniques are too laborious and time consuming.

It is thus imperative that routine activation analysis should be performed possibly without chemical separation and that the maximum possible sensitivity should be obtained in the minimum possible time.

A general method is given in the following for the calculation of the optimum activation and subsequent cooling time before the measurement is started, if one wants to keep the relative error in the measured value of the activity in question at a minimum, when the measurement is performed by scintillation spectrometer and besides the background there is some interfering activity present. The calculated values of relative accuracy and maximum possible sensitivity for various times of measurement are then given. A computer program from another, but not quite correct starting point for the same problem was given by ISENHOUR and MORRISON [1].

The application of this method permits to see if there is any necessity of additional chemical separation even in the case of optimum scheduled operations.

Evaluation of the optimum activation and cooling time

In the calculations the following symbols are used:

m_i = quantity of activated material, grams

M_i = atomic weight

τ_i = half-life

P_i = isotopic abundance

where the indices $i = 1$ or 2 stand for the interference and analyzed activities, respectively. Let σ_i be the activation cross-section of the investigated elements in barns then the nuclei activated by exposure to a neutron flux of Φ neutron/cm^2/sec for time T' and subsequently cooled for time t' will yield in the activity measurement a disintegration per sec given by

$$A_i = \Phi m_i P_i \sigma_i \frac{0.602}{M_i} (1 - 2^{-T'/\tau_i})\, 2^{-t'}/\tau_i .$$

For simplicity we put

$$B'_i = \Phi m_i P_i \sigma_i \frac{0.602}{M_i} ; \quad T = T'/_{\tau 1,} ; \quad t = t'/_{\tau 1} : \quad x = \tau_1/\tau_2 ;$$

$B_i = B'_i R_i$ (for the definition of R_i see later)
and the instantaneous activites can be expressed as

$$A_1 = B'_1 (1 - 2^{-T})\, 2^{-t}; \quad A_2 = B'_2 (1 - 2^{-Tx})\, 2^{-tx}. \tag{1}$$

First we considered the case when there is no appreciable decrease in the activities measured over time τ, that is

$$4\tau < \tau_i . \tag{2}$$

The number of counts on the full energy peak of the element to be determined is then given by

$$N_2 = A_2 R_2 \tau (1 - 2^{-Tx})\, 2^{-tx}, \tag{3a}$$

where R_2 is the probability of a photopeak count for the emitted γ-quantum and the detector used [2].

If the measured activity has a higher energy γ-line than the interfering one, overloading of the detector and superposition on the low energy pulses has to be prevented. This can be usually achieved by appropriate geometry. This case, or that of an overlapping of the measured and interfering full energy peaks will not be considered here, since in the latter case identification of the measured spectra has to be done by means of a computer.

The case of present interest is in which the photopeak of the measured activity lies in the Compton range of the interfering line. The counting rate of the latter contributing to the photopeak of the activity to be measured is then given by

$$N_1 = A_1 R_1 \tau = B_1 \tau (1 - 2^{-T})\, 2^{-t}, \tag{3b}$$

where R_1 is the probability of an interference count in the energy range in question. The approximate counting probabilities at 100 keV of the Compton spectrum (average width of a full energy peak) for γ-radiations of various energies and for various measuring set-ups, can be read from Figure 1/a and 1/b. The calculations were performed on CROUTHAMEL's data [2], and on HEATH's spectrum catalogue [5]. The results are valid in the energy region ranging from the end of the backscattering peak till the beginning of the COMPTON edge; for every shielding, if the walls of the shielding box are faster than few inches from the crystal. The background intensity H in the photopeak counts is assumed over time τ to be constant

$$N_3 = H\tau. \tag{3c}$$

The maximum possible accuracy of the determination obtainable without chemical separation depends in principle only on the statistical deviation of the measured activity of the sample, provided other errors in the standards, irradiated and measured under identical conditions, are negligible.

Considering the Poissonian distribution of the counting rates, the relative accuracy in the determination is given by the formula

$$\delta = \frac{N_2}{\sqrt{2N_1 + N_2 + 2N_3}} = \sqrt{\tau}\,\frac{B_2(1-2^{-Tx})\,2^{-tx}}{\sqrt{B_2(1-2^{-Tx})\,2^{-tx} + B_1(1-2^{-T})\,2^{-t} + H}} \tag{4}$$

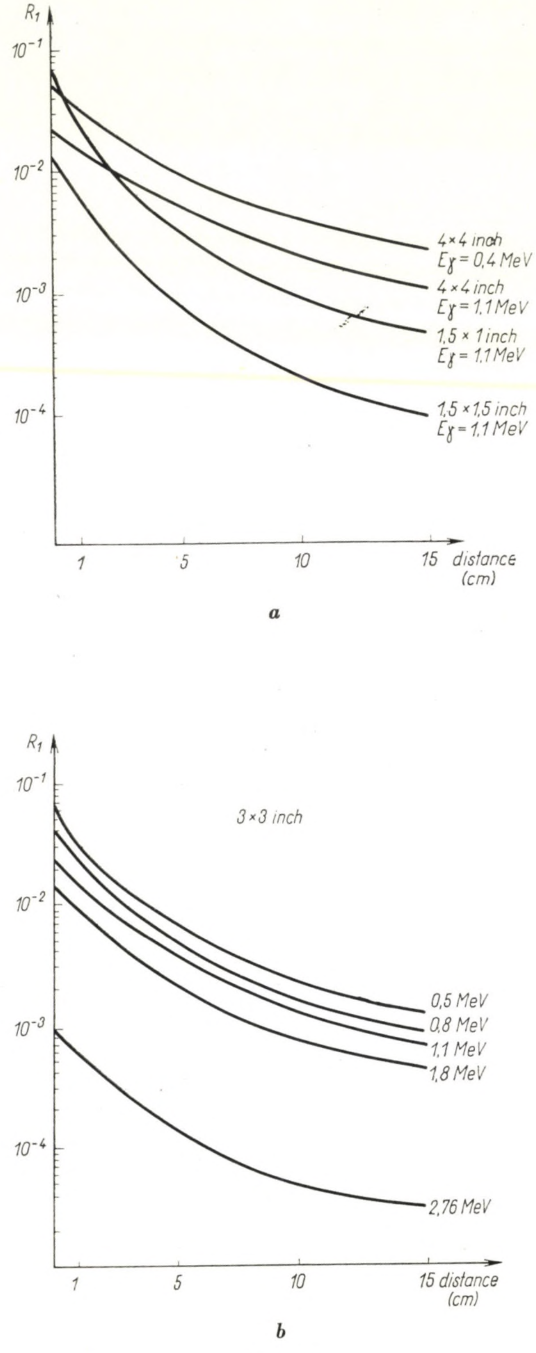
where N_2 is the difference between the total number of counts $(N_1 + N_2 + N_3)$ and the background plus interfering activity $(N_1 + N_3)$ [6]. The counts, due to the interfering activity are estimated from the extrapolation of the Compton region of its known spectrum.

One can see that the relative accuracy increases proportionally to the square root of the measuring time. Since for practical reasons and because of (2) it cannot be of any length, actually it does not affect the choice of the irradiation and cooling schedule, it is assumed to be given.

Now we have to evaluate T and t such as to obtain the maximum for Eq. (4).

It can be shown if $x = \frac{\tau_1}{\tau_2} \geq 0.5$, (4) will be at a maximum for $t = 0$. Thus, if the half-life of the interfering activity is as much as half that of the analyzed activity, or more, it is reasonable to start with the activity measurement immediately after the irradiation. Writing $t = 0$ into Eq. (4), it becomes apparent that for $x = 0.5$ we have $T' = \infty$ as it is obvious for other reasons, too.

If $x > 1$, by introducing the notation $y = 2^{-T}$, (4) will be at a maximum, considering the requirement $\frac{\partial\delta}{\partial y} = 0$, determined by the root y_0 in the interval


R_1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
4×4 inch E_γ = 0,4 MeV
4×4 inch E_γ = 1,1 MeV
1,5 × 1 inch E_γ = 1,1 MeV
1,5 × 1,5 inch E_γ = 1,1 MeV
1
5
10
15 distance (cm)
R_1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
3×3 inch
0,5 MeV
0,8 MeV
1,1 MeV
1,8 MeV
2,76 MeV
1
5
10
15 distance (cm)

a

b

Fig. 1

[0; 1] of the equation

$$B_2 x y^{2x-1} + 2B_1 (2x - 1) y^x + 2B_1 - x y^{x-1} (4B_1 + 4H + B_2) = 0. \tag{5}$$

Knowing this root, the optimum irradiation time is given by

$$T'_{opt} = - \frac{\tau_1 \ln y_0}{\ln 2}. \tag{6}$$

Eq. (5) need not be solved in each case, since for $y \ll 1$, the terms with y^x, y^{2x-1} can be neglected, thus we have

$$y_0 \cong \sqrt[x-1]{\frac{2B_1}{(4B_1 + 4H + B_2) x}},$$

hence T'_{opt} is determined by the expression:

$$T'_{opt} = \frac{\tau_1}{(x - 1) \ln 2} \cdot \ln \frac{x (4B_1 + 4H + B_2)}{2B_1}. \tag{7}$$

This approximation holds in the interval $1 < x < 3$ but for $B_2 \geq B_1$, it yields a satisfactory value also for $x > 3$.

If $x < 0.5$, then $T_{opt} = \infty$ (this is physically obvious, since saturation activity takes a longer time to set in for longer lived activities). Making now the substitution into (4) and introducing $z = 2^{-t}$, the optimum cooling time will be determined by the root z_0 in the interval [0; 1] of the equation

$$B_2 x z^x + 2B_1 (2x - 1) z + 4x H = 0 \tag{8}$$

In the special case if $x \ll 1$, we have $z^x \approx 1$, thus

$$z_0 \cong \frac{x (B_2 + 4H)}{2B_1 (1 - 2x)}$$

hence

$$t'_{opt} = - \frac{\tau_1 \ln z_0}{\ln 2} = \frac{\tau_1}{\ln 2} \ln \frac{2B_1 (1 - 2x)}{x (B_2 + 4\mathrm{H})} \tag{9}$$

The value of z_0 will be equal to unity, if

$$x = 0.5 - \frac{B_2 + 4H}{2B_2 + 8B_1 + 8H} = x_1 \tag{10}$$

thus, if $x > x_1$, Eq. (8) will have no root in the interval [0; 1] and $z_0 > 1$, hence $t'_{opt} = 0$.

The maximum possible relative accuracy can be evaulated by substituting the thus calculated values of the measuring and cooling time into Eq. (4).

The results obtained, keeping in mind that the required sensitivity should be attained within the minimum possible measuring time, are summarized in Table I.

The numerical solutions of (5) and (8) were obtained on a computer. The results are plotted for different half-lives, H/B_2 and B_1/B_2 ratios in Fig. 2—4.

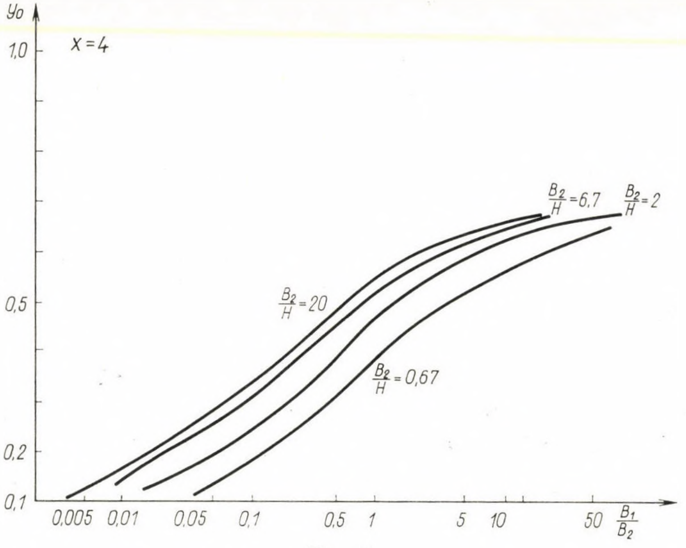


Fig. 2

Now, let us consider the case when condition (2) is not satisfied, restricting the investigation to the case when $\tau_1 \gg \tau_2 < 4\tau$, since for $\tau_2 \gg \tau_1 \sim \tau$ after the decay of the interfering activity the measurement becomes very simple.

For $\tau_1 \sim \tau_2$ (with any τ), the measured and interfering activities having the same decay time and the background being negligible, the relative accuracy is given instead of

$$\delta = \frac{B_2}{\sqrt{2B_1 + B_2 + 2H}}\,, \text{ by } \delta = I \frac{B_2}{\sqrt{2\,B_1\,x + B_2 + \dfrac{H}{I}}}\,, \text{ where}$$

$$I = \frac{\tau_2\,(1 - 2^{-\tau}/\tau_2)}{\ln 2}\,,$$

In this case the values of T' and t' can be determined with the assumption of a given value of τ. The number of counts N_2 is given by $N_2 = A_2(1-e^{-\Theta})$, where $\frac{\ln 2}{\tau_2} A_2$ is the counting rate at the start of the measurement. Here $\Theta = (\ln 2)\tau/\tau_2$.

If N_1 is the counting rate due to all the interfering activities, it can be expressed by considering the given conditions also in the form $N_1 = C' \tau = C\Theta$.

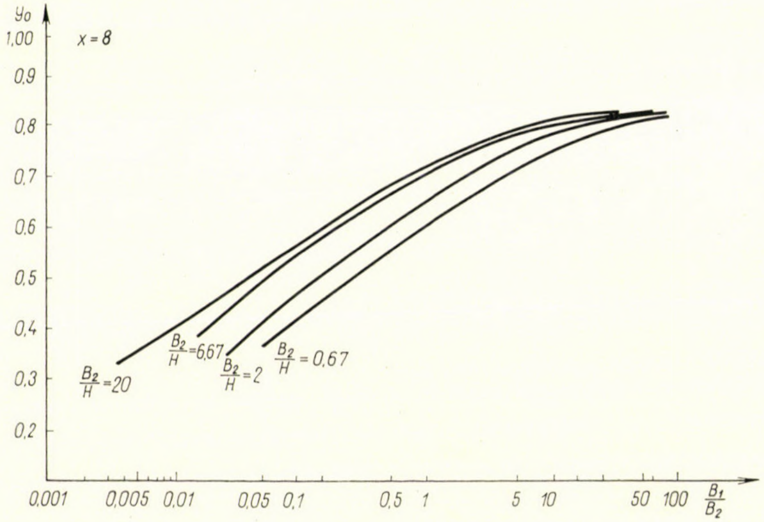


Fig.

Table I

$x = \tau_1/\tau_2$		T'opt	t'opt	rel. accuracy
$x \ll 1$		∞	$\frac{\tau_1}{\ln 2} \ln \frac{B_1(1-2x)}{x(B_2+2H)}$	exp. (4)
$x < 0.5$	$x < x_1$	∞	solution of the Eq. (8)	exp. (4)
	$x > x_1$	∞	0	$\sqrt{\tau}\,\frac{B_2}{\sqrt{2B_1+B_2+2H}}$
$0.5 < x < 1$		∞	0	$\sqrt{\tau}\,\frac{B_2}{\sqrt{2B_1+B_2+2H}}$
$1 < x < 3$		$\frac{\tau_1}{(x-1)\ln 2} \ln \frac{x(4B_1+4H+B_2)}{2B_1}$	0	exp. (4)
$3 < x$		solution of the Eq. (5)	0	exp. (4)

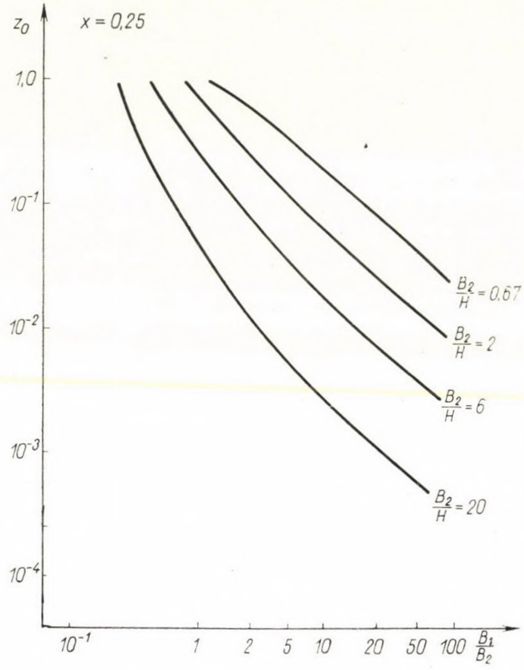


Fig. 4

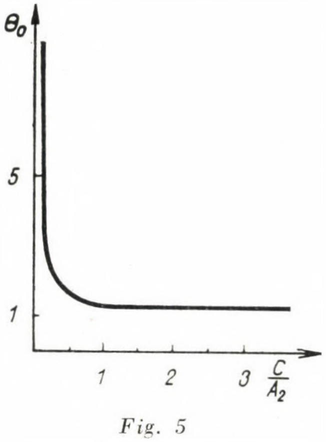


Fig. 5

The relative error in the counting rate N_2 of the activity we want to measure is then

$$\Delta(\Theta) = \frac{\delta(N_1 + N_2) + \delta N_1}{N_2} = \frac{\sqrt{2N_1 + N_2}}{N_2},$$

the minimum value of which is determined by the root Θ_0 of the equation

$$\frac{1 - e^{-\Theta}}{e^{\Theta} - (2\theta + 1)} = \frac{2C}{A_2},$$

where C/A_2 is the ratio of the background and the activity to be measured at the beginning of the measurement. From this equation the optimum measuring time is given as $\tau_{opt} = \frac{\tau\, 2\, \Theta_0}{\ln 2}$.

The results of the calculations are shown in Fig. 5. It is apparent that as long as the counting rate of the background exceeds that of the activity to be measured, it is reasonable to choose the measuring time to be about 2 τ_2. For a subsequent decrease in background counts, the optimum of the measuring time shows a rapid increase.

Application of the method

The optimum conditions for an actual measurement can be determined as follows.

The value of $x = \tau_1/\tau_2$ is calculated from the half-lives. the B_1-s from the numerical data (2) (3) (4). The values of T' and t' are then computed from Equations (5) to (10).

These calculations permit also to establish the minimum detectable impurity, if there is a known amount of interfering activity present.

The result of a measurement is significant only if the value of N_2 exceeds by a factor of 3 the statistical deviation of the counting rate $N = N_1 + N_3$ due to all the interfering activities present. It follows that the minimum detectable quantity is given by

$$m_{min} = \frac{3}{\sqrt{\tau}} \cdot \frac{\sqrt{H + B_1 (1 - 2^{-T}) \cdot 2^{-t}}}{\frac{\Phi p_2 \sigma_2 \cdot 0.602}{M_2} (1 - {}^{-Tx}) \cdot 2^{-tx}}. \tag{11}$$

For illustration, let us see an example.

We want to detect 10^{-9} g Cu in the presence of 10^{-8} g Na, using 3″ × 3″ NaI(Tl) crystal at 6 cm from radiation source. The thermal neutron flux used for activation is 10^{13} cm^{-2} sec^{-1}. Neither the matrix element nor its decay products are assumed to emit γ-rays upon activation. If this is not so, a correction has to be applied.

In the above case $\tau_1 = 15\ h$; $\tau_2 = 12.8\ h$; $x = 1.17$. It is seen that it is easy to meet the requirement $4\tau < \tau$, by choosing the measuring time to be, *e.g.* 3600 sec. The ^{65}Cu activity does not interfere with the measurement, since it disappears after 20 min.

Considering the decay scheme of ^{24}Na, we have to deal with the coincidence of 2.76 MeV and 1.37 MeV photons. The probability of their simultaneous detection being about negligible, the probabilities of their counts in the 100 keV interval of the COMPTON range are expressed individually and then summed.

The measurement covers the 511 keV photopeak of Cu, considering that only 19% of the total acitivity is due to positrons.

The conditions are chosen to be such that the background counts in the covered range yield $H = 3$ c. p. s. From the numerical values (2) (3) (4) $B_1 = 3.02$ and $B_2 = 1.66$; thus, from (5) and (6) we have $T'_{opt} = \cong 200$ h and from (4) $\delta = 27$.

The maximum possible sensitivity is then by (11) $2 \cdot 10^{-11}$ g Cu.

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A NEW METHOD FOR THE CALCULATION OF STABILITY CONSTANTS

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Studies of equilibria of complexes afford very often the experimental formation curve corresponding to the function $\bar{n} = f(pA)$. To calculate the stability constants from these data, various graphic methods have been developed by a number of authors. The most wide-spread ones are: the correction term method introduced by Irving and Rossotti [1], Rossotti's [2] extrapolation method, Sillén's [3] method of curve fitting and the projection-strip procedure reported by Rossotti and Sillén [4]. With the correction term method, for the case of $N = 2$ (and with some restriction also for $N = 3$), accurate constants can be obtained if we have nearly the whole formation curve at our disposal, and if it is symmetric about the midpoint. This condition, however, cannot always be fulfilled. Thus, for example, the formation curves of Cu(II)-α-amino acid systems are sometimes not symmetrical. This is mostly due to the circumstance (if the experimental data are obtained pH-metrically) that the error of pH-measurement is reflected, in the data obtained, squared for the $\bar{n} < 1$ section of the curve, and on the first power for the section $\bar{n} > 1$. In connection with this it should be noted that, in numerous cases, such equilibrium systems are involved for which log K_1/K_2 ranges approximately from 0.8 to 1.3. Under such conditions however, from the nomogram constructed by Irving and Rossotti, the correction terms referring to the points $\bar{n} = 1 \pm 0.1$ and $\bar{n} = 1 \pm 0.2$ of the function can only be read with an inaccuracy of several hundreths. Accordingly, if the formation curve is symmetrical only in the section about $\bar{n} \cong 1$, the constants obtained give only an accuracy of several hundredths of $\log K$. The error referred to above and due partly to the inaccuracy of the formation curve can be estimated by the application of the projection strip method. Nevertheless, at low values of log K_1/K_2, if we do not have nearly the whole of the formation curve at our disposal, we can calculate the stability constants, even by the projection strip method, with no less error than mentioned above.

Furthermore, there are systems for which the correction term method cannot be applied to calculate the stability constants at all. Among others the Cd(II)- and the Co(II)-α-amino acid systems fall in this group, for which the formation curve is sometimes well defined up to $\bar{n} \cong 1.2$ only.

With the curve fitting and the extrapolation methods (the former is more accurate) the constants can be similarly obtained with an accuracy of some hundredths of log K. These constants are sufficiently accurate for a number of purposes. They cannot be employed, however, in the case when we wish to determine, *e. g.* with the temperature coefficient method, the enthalpy changes of complex-forming processes.

The use of computers has recently made possible to calculate highly accurate constants. Since they are not generally wide-spread yet, the present work aims at elaborating a new method that enables us to obtain, from the experimental data, the logarithms of the constants with a maximum error of 0.01 log K. This aim is essentially achieved by a modification of the correction term method, starting with FRONAEUS' [5] expression.

Descripton of the principle of the modified correction term method

Part of the graphic procedures referred to above is based on the relation that, on the one hand, the formation function

$$\bar{n} = \frac{K_1[A] + 2K_1K_2[A]^2}{1 + K_1[A] + K_1K_2[A]^2} \tag{1}$$

is symmetric for $\bar{n} = 1$, while the shape of the formation curve is determined by the K_1/K_2 ratio. In our considerations, besides the former, we started with the assumption that the size of the area defined by any given two points of the formation curve only depends, apart from $\bar{n}$, on the ratio, K_1/K_2.

To prove the above assumption, FRONAEUS' [5] expression was chosen as the starting point.

$$\int\limits_{pA_0}^{pA\bar{n}} \bar{n}dpA = \Big[-\log(1 + K_1[A] + K_1K_2[A]^2)\Big]_{0}^{A\bar{n}} \tag{2}$$

The values of $[A]$ and $[A]^2$ included in expression (2) are given by the inverse function of Eq. (1), or the square thereof, respectively:

$$[A] = \frac{(1-\bar{n})K_1 - \sqrt{(\bar{n}-1)^2K_1^2 + 4\bar{n}(2-\bar{n})K_1K_2}}{2(\bar{n}-2)K_1K_2} \tag{3}$$

$$[A]^2 = \frac{(1-\bar{n})^2K_1^2 - 2(1-\bar{n})K_1\sqrt{(\bar{n}-1)^2K_1^2 - 4\bar{n}(\bar{n}-2)K_1K_2}}{4(\bar{n}-2)^2K_1^2K_2^2} + \frac{(\bar{n}-1)^2K_1^2 - 4\bar{n}(\bar{n}-2)K_1K_2}{4(\bar{n}-2)^2K_1^2K_2^2} \tag{4}$$

Substituting (3) and (4) into (2), and with the simplifications, we get:

$$\int_{pA_0}^{pA\bar{n}} \bar{n}dpA = \log \left[1 + \frac{\bar{n}}{2-\bar{n}} + \frac{\bar{n}-1}{2(\bar{n}-2)^2}\frac{K_1}{K_2} + \right.$$

$$\left. + \frac{1}{2(\bar{n}-2)}\sqrt{(\bar{n}-1)^2\left(\frac{K_1}{K_2}\right)^2 - 4\bar{n}(\bar{n}-2)\frac{K_1}{K_2}}\right] \tag{5}$$

Thus, our initial assumption has been proved, since the area defined determined by two points of the formation curve, apart from $\bar{n}$, really depends on the ratio K_1/K_2 only.

By means of relation (5), with $\bar{n} = 0.1$ to 1.9 and changing the $\log (K_1/K_2)$ ratio from 0 to 4 by intervals of 0.2, the corresponding areas have been calculated. These values are listed in Table I.

On the basis of the data in Table I, values of areas belonging to the most frequently occurring $\log K_1/K_2$ ratios are summed up, between various $\bar{n}_1$ and $\bar{n}_2$ limits, in Table II and represented in Fig. 1.

As it follows from what has been said above, graphically integrating the area belonging to two points of the formation curve, the $\log K_1/K_2$ ratio pertaining to these values can be read from Fig. 1. With this ratio known, the constants can be calculated at several points of the curve by means of the relations established by IRVING and ROSSOTTI [1]:

$$\log K_1 = pA_{1-d} + y \tag{6}$$

$$\log K_2 = pA_{1+d} - y \tag{7}$$

$$\Delta pA_d = pA_{1-d} - pA_{1+d} = \log \frac{K_1}{K_2} - 2y \tag{8}$$

Provided that we have at our disposal the section of the formation about $n \cong 1$, and $\log (K_1/K_2)$ is known y can be accurately calculated from Eq. (8). If no section of the formation curve under $\bar{n} = 1$, or above $\bar{n} = 1$ can be experimentally obtained, the y values given by IRVING and ROSSOTTI may be used in the calculations. However, since these authors calculated the values of y by changing $\log K_1/K_2$ by intervals of about 0.5, in order to increase accuracy, we have calculated some correction terms belonging to other $\log K_1/K_2$ ratios, too. The results are listed in Table III and represented in Fig. 2.

Application of the modified correction term method will be demonstrated on the examples of the systems Cu(II)-glycine and Ni(II)-glycine. The enthalpy and entropy changes of complex-forming processes will be calculated from the stability constants obtained at various temperatures.

Table I

Relation between log K_1/K_2 and the

$\log \frac{K_1}{K_2}$:	0.0	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
n	$\int_0^{\bar{n}} \bar{n}dpA$									
0.1	0.0420	0.0431	0.0439	0.0446	0.0450	0.0452	0.0454	0.0455	0.0456	0.0457
0.2	0.0829	0.0863	0.0892	0.0915	0.0932	0.0945	0.0953	0.0957	0.0962	0.0965
0.3	0.1240	0.1304	0.1361	0.1411	0.1451	0.1482	0.1504	0.1520	0.1530	0.1537
0.4	0.1663	0.1759	0.1852	0.1937	0.2011	0.2071	0.2117	0.2150	0.2174	0.2189
0.5	0.2003	0.2234	0.2368	0.2497	0.2616	0.2719	0.2803	0.2867	0.2914	0.2947
0.6	0.2565	0.2735	0.2915	0.3096	0.3272	0.3434	0.3574	0.3689	0.3778	0.3844
0.7	0.3056	0.3268	0.3498	0.3739	0.3984	0.4223	0.4445	0.4640	0.4803	0.4931
0.8	0.3582	0.3839	0.4124	0.4434	0.4761	0.5096	0.5428	0.5743	0.6029	0.6276
0.9	0.4150	0.4456	0.4803	0.5189	0.5610	0.6062	0.6534	0.7016	0.7494	0.7955
1.0	0.4771	0.5132	0.5545	0.6015	0.6544	0.7128	0.7767	0.8458	0.9196	0.9975
1.1	0.5458	0.5877	0.6365	0.6930	0.7575	0.8308	0.9132	1.0052	1.1076	1.2207
1.2	0.6227	0.6712	0.7284	0.7951	0.8725	0.9614	1.0628	1.1773	1.3056	1.4474
1.3	0.7105	0.7665	0.8329	0.9110	1.0020	1.1070	1.2267	1.3512	1.5098	1.6713
1.4	0.8126	0.8772	0.9542	1.0447	1.1493	1.2612	1.4076	1.5587	1.7225	1.8968
1.5	0.9348	1.0097	1.0986	1.2030	1.3234	1.4599	1.6113	1.7756	1.9505	2.1333
1.6	1.0869	1.1741	1.2771	1.3966	1.5326	1.6837	1.8481	2.0230	2.2060	2.3946
1.7	1.2876	1.3904	1.5100	1.6463	1.7981	1.9630	2.1385	2.3219	2.5108	2.7036
1.8	1.5701	1.7033	1.8433	1.9983	2.1661	2.3438	2.5287	2.7188	2.9124	3.1082
1.9	2.1060	2.2584	2.4241	2.6002	2.7841	2.9734	3.1665	3.3620	3.5592	3.7574

Table II

Area-values belonging to the most frequent ratios of log K_1/K_2 between various $\bar{n}_1$ and $\bar{n}_2$ limits

$\log \frac{K_1}{K_2}$	0.4	0.6	0.8	1.0	1.2	1.4
$\bar{n}_1 - \bar{n}_2$	area					
0.3—1.0	0.4184	0.4604	0.5093	0.5646	0.6263	0.6938
0.6—1.2	0.4396	0.4855	0.5453	0.6180	0.7054	0.8084
0.7—1.3	0.4831	0.5371	0.6036	0.6847	0.7822	0.8872
0.6—1.3	0.5414	0.6010	0.6748	0.7636	0.8693	0.9823
0.5—1.5	0.8618	0.9533	1.0618	1.1880	1.3310	1.4889
0.4—1.6	1.0919	1.2029	1.3315	1.4766	1.6364	1.8080

areas belonging to given values of $\bar{n}$

2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.0
$\int_0^{\bar{n}} \bar{n} dpA$										
0.0457	0.0457	0.0457	0.0457	0.0458	0.0458	0.0458	0.0458	0.0458	0.0458	0.0458
0.0967	0.0968	0.0968	0.0968	0.0969	0.0969	0.0969	0.0969	0.0969	0.0969	0.0969
0.1541	0.1544	0.1546	0.1547	0.1548	0.1548	0.1549	0.1549	0.1549	0.1549	0.1549
0.2200	0.2207	0.2211	0.2214	0.2216	0.2217	0.2217	0.2218	0.2218	0.2218	0.2218
0.2969	0.2984	0.2993	0.2999	0.3003	0.3006	0.3008	0.3009	0.3009	0.3010	0.3010
0.3890	0.3917	0.3942	0.3956	0.3964	0.3970	0.3973	0.3975	0.3977	0.3978	0.3978
0.5026	0.5094	0.5141	0.5172	0.5192	0.5206	0.5214	0.5219	0.5223	0.5225	0.5226
0.6478	0.6634	0.6749	0.6831	0.6886	0.6923	0.6947	0.6964	0.6973	0.6980	0.6983
0.8381	0.8762	0.9085	0.9346	0.9547	0.9694	0.9797	0.9868	0.9915	0.9946	0.9965
1.0792	1.1640	1.2516	1.3415	1.4333	1.5266	1.6213	1.7170	1.8136	1.9108	2.0086
1.3452	1.4815	1.6296	1.7889	1.9584	2.1364	2.3210	2.5107	2.7038	2.8994	3.0965
1.6021	1.7682	1.9439	2.1271	2.3159	2.5085	2.7034	2.9003	3.0983	3.2970	3.4962
1.8435	2.0242	2.2111	2.4025	2.5969	2.7933	2.9909	3.1895	3.3885	3.5879	3.7876
2.0792	2.2674	2.4596	2.6546	2.8514	3.0493	3.2480	3.4472	3.6467	3.8463	4.0461
2.3219	2.5144	2.7095	2.9064	3.1044	3.3032	3.5024	3.7019	3.9016	4.1014	4.3012
2.5872	2.7825	2.9794	3.1774	3.3762	3.5754	3.7749	3.9746	4.1743	4.3742	4.5742
2.8990	3.0960	3.2941	3.4930	3.6922	3.8917	4.0914	4.2912	4.4910	4.6909	4.8909
3.3056	3.5038	3.7029	3.9022	4.1018	4.3015	4.5013	4.7012	4.9011	5.1011	5 3011
3.9562	4.1555	4.3550	4.5547	4.7545	4.9544	5.1544	5.3543	5.5543	5.7543	5.9543

Table III

Relation between y and log (K_1/K_2) at various values of d

d / $\log \frac{K_1}{K_2}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
	y								
0.523	0.178	0.093	0.004	—0.085	—0.196	—0.317	—0.465	—0.662	—0.980
0.650	0.235	0.144	0.049	—0.053	—0.164	—0.291	—0.445	—0.649	—0.974
0.820	0.310	0.209	0.105	—0.006	—0.127	—0.262	—0.424	—0.635	—0.969
1.00	0.388	0.274	0.159	0.036	—0.094	—0.238	—0.407	—0.625	—0.964
1.180	0.462	0.334	0.204	0.071	—0.068	—0.220	—0.395	—0.617	—0.961
1.350	0.529	0.383	0.242	0.098	—0.049	—0.207	—0.387	—0.612	—0.959
1.523	0.593	0.430	0.273	0.120	—0.035	—0.198	—0.381	—0.609	—0.957

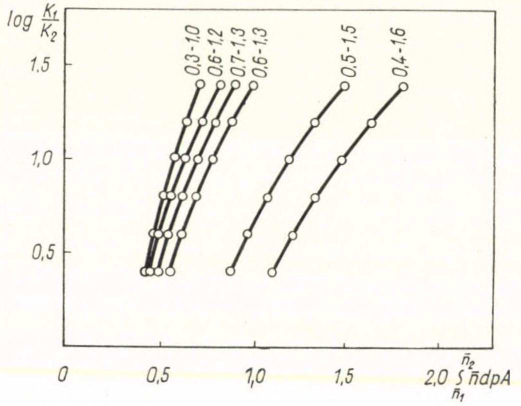

Fig. 1. Ratio of the logarithm of the stability constants within different $\bar{n}_1$ and $\bar{n}_2$ limits, plotted as a function of the area

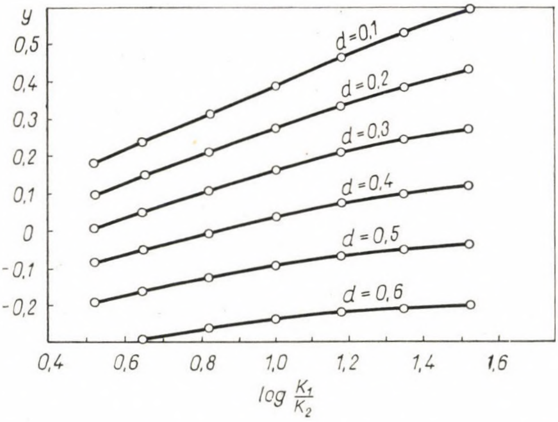

Fig. 2. The Irving—Rossotti correction term (y) at different values of d plotted as a function of log (K_1K_2)

Experimental

Instruments and reagents

The pH-metric titrations were carried out at 20°, 25° and 30 °C with a *Radelkis Type OP* 204 titriscope, with calibrated glass- and saturated electrodes in nitrogen atmosphere. The accuracy of pH measurements was ± 0.01 pH-unit. Temperature was maintained constant within ± 0.1 °C by an ultrathermostat. Glycine, of analytical grade *(Merck)* was used. The Cu(II) and Ni(II) stock solutions were prepared from metal nitrates of analytical purity, concentrations were checked gravimetrically. Ionic strength was adjusted to 0.1 with KNO_3 solution. For the titrations CO_2-free 0.25 *N* NaOH solution was used.

The buffers used to standardize the pH-meter were chosen so that their values should be near the pH changes occurring in the course of titration.

In each case at least four parallel titrations were made.

Determination of the acid dissociation constants of glycine

Although for the acidic dissociation constants of glycine a number of data can be found in the literature [6], it was necessary to re-determine them. For this purpose $1.00 \cdot 10^{-2}$ mole/l glycine solutions, also containing one equivalent perchloric acid, were titrated with alkali. (To standardize the pH-meter, in this case, citric acid and borax buffers were applied.)

The calculations were performed numerically to give the following results:

$-\log K_{12} = 2.52$, $-\log K_1 = 9.84$ (at 20°); $-\log K_{12} = 2.51$
$-\log K_1 = 9.70$ (at 25°); $-\log K_{12} = 2.50$, $-\log K_1 = 9.60$ (at 30°).

Evaulation of the formation curves

$1.00 \cdot 10^{-2}$ mole/l glycine solutions containing $5.00 \cdot 10^{-3}$ mole/l of Cu(II) and $3.31 \cdot 10^{-3}$ mole/l of Ni(II) were titrated with alkali. The formation curves were calculated by means of the relations published by ALBERT [7]. (To standardize the pH-meter, for Cu(II) we used potassium hydrogen phtalate, for Ni(II), a phosphate buffer.)

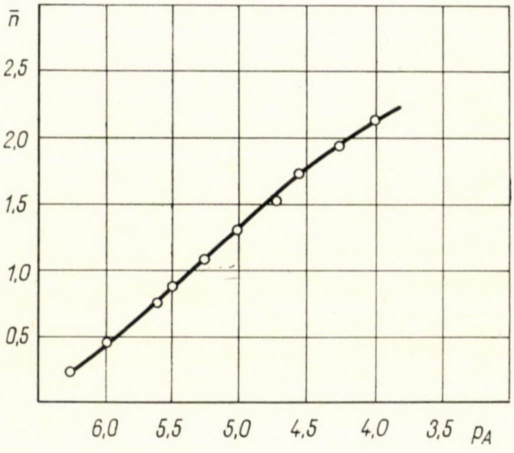

Fig. 3. Formation curve of the system Ni(II)-glycine at 20 °C

Results and discussion

Calculation of the stability constants with the modified correction term method

Constants of Ni(II)-glycine complexes

The modified method is best applicable if the maximum coordination number is two. Satisfactory accurate constants can also be obtained for Ni(II)-α-amino acid systems, if the data up to $\bar{n} = 1.2$ are used for the calculations, because in this case hardly any or absolutely no complex of the type MA_3 is formed.

Fig. 3 shows the formation curve of Ni(II)-glycine obtained at 20°.

The formation curve was graphically integrated between the limits $\bar{n} = 0.6$ and $\bar{n} = 1.2$. The area was 0.580, for which the corresponding log (K_1/K_2)

is 0.896, according to Fig. 1. From the latter value, log K_1 and K_2 for the middle of the formation curve can be obtained in the following way:

$$y = \frac{1}{2} \log \left(\frac{K_1}{K_2} \right) \tag{9}$$

and since at this point

$$2\, pA = \log\ (K_1 K_2) \tag{10}$$

thus,

$$\log K_1 = \frac{1}{2} \log (K_1 K_2) + \frac{1}{2} \log \left(\frac{K_1}{K_2} \right) \tag{11}$$

and

$$\log K_2 = \frac{1}{2} \log\ (K_1 K_2) - \frac{1}{2} \log \left(\frac{K_1}{K_2} \right) \tag{12}$$

In the section $0.7 > \bar{n} < 1.3$ of the formation curve, when log (K_1/K_2) is known, the correction terms y may be calculated by means of Eq. (8) from the relation

$$y = \frac{1}{2} \log \left(\frac{K_1}{K_2} \right) - \frac{\Delta pA_d}{2} \tag{13}$$

while the y values corresponding to $\bar{n} < 0.8$ $(d > 2)$ were read from Fig. 2. Thus, knowing pA_{1-d} by Eq. (7) we can get log K_1, while log K_2 is obtained from the relation

$$\log K_2 = \log K_1 - \log \left(\frac{K_1}{K_2} \right) \tag{14}$$

The results of these calculations are given in Table IV.

Table IV

Calculation of the stability constants of the system Ni(II)-glycine at 20°

d	pA_{1-d}	pA_{1+d}	$\frac{\Delta pA_d}{2}$	y	log K_1	log K_2
0.0	5.34	5.34	0.00	0.448	5.79	4.89
0.1	5.44	5.24	0.10	0.348	5.79	4.89
0.2	5.56	5.14	0.21	0.238	5.80	4.90
0.3	5.67	—	—	0.125	5.79	4.90
0.4	5.79	—	—	0.015	5.81	4.91
0.5	5.92	—	—	—0.110	5.81	4.91
				Mean:	5.80	4.90

Quite similarly we also calculated the stability constants of the Ni(II)-glycine complexes from the formation curves obtained at 25° and 30°. To check the constants, the values of $\bar{n}$ were re-calculated by means of expression (1) of the formation curve. The corresponding log K_1 and log (K_1K_2), pA, $\bar{n}_{\text{exp.}}$ and $\Delta\bar{n} = (\bar{n}_{\text{exp.}} - \bar{n}_{\text{calc.}})$ are summarized in Table V.

Table V

Differences between the experimental and calculated $\bar{n}$ values of the Ni(II)-glycine system at 20°, 25° and 30°

20°; $\log(K_1/K_2) = 0.896$; $\log K_1 = 5.80$; $\log(K_1K_2) = 10.70$; $\sigma = \pm 0.008$

pA	5.981	5.861	5.612	5.378	5.272	5.036
$\bar{n}_{\text{expt.}}$	0.435	0.544	0.757	0.978	1.087	1.304
$\Delta\bar{n}$	+0.014	—0.0043	—0.0028	—0.003	—0.011	—0.008

25°; $\log(K_1/K_2) = 0.90$; $\log K_1 = 5.73$; $\log(K_1/K_2) = 10.56$; $\sigma = \pm 0.01$

pA	6.010	5.800	5.580	5.400	5.214	5.050
$\bar{n}_{\text{expt.}}$	0.365	0.532	0.709	0.886	1.064	1.235
$\Delta\bar{n}$	+0.016	+0.002	—0.01	—0.0003	—0.001	—0.015

30°; $\log(K_1/K_2) = 0.93$; $\log K_1 = 5.70$; $\log(K_1K_2) = 10.47$; $\sigma = \pm 0.007$

pA	5.891	5.741	5.492	5.258	5.132	4.916
$\bar{n}_{\text{expt.}}$	0.435	0.544	0.759	0.978	1.087	1.304
$\Delta\bar{n}$	+0.0034	+0.0066	+0.0042	+0.0014	+0.010	—0.010

Constants of Cu(II)-glycine complexes

The formation curves for the system Cu(II)-glycine were graphically integrated between the limits of $\bar{n} = 0.5$ and $\bar{n} = 1.5$. In this case, however, having obtained log (K_1/K_2), the correction terms y were calculated at each considered experimental point by means of Eq. (13). The rest of the procedure was exactly the same as with the system Ni(II)-glycine. The stability constants obtained at various temperatures and the data for pA, $\bar{n}_{\text{exp.}}$ and $\Delta\bar{n}$ were summed up in Table VI. From Tables V and VI it can be seen that the new method of calculation gave really constants satisfying the formation curves. For the systems Cu(II)-glycine and Ni(II)-glycine the constants are in agreement with the data found in the literature [6]. We have fairly good agreement with the highly accurate data of ANDEREGG [8], obtained at 20° in 0.1 N $NaNO_3$, similarly pH-metrically, but with a computer. The constants obtained by the above author were for Ni(II)-glycine: log $K_1 = 5.82$, log $K_2 = 4.82$; for Cu(II)-glycine: log $K_1 = 8.183$, log $K_2 = 6.921$. The differences between our data and those of ANDEREGG amount to about 0.1 log K.

Table VI

Differences between the experimental and the calculated $\bar{n}$ values of the Cu(II)-glycine system at 20°, 25° and 30°

20°; $\log (K_1/K_2) = 1.263$; $\log K_1 = 8.313$; $\log (K_1K_2) = 15.363$; $\sigma = \pm 0.005$

pA	8.515	8.332	8.137	8.030	7.815	7.570	7.325	7.197	7.065
$\bar{n}_{exp.}$	0.415	0.525	0.670	0.738	0.905	1.080	1.265	1.355	1.455
$\Delta\bar{n}$	−0.008	+0.002	−0.005	+0.006	−0.003	+0.002	−0.003	+0.001	−0.003

25°; $\log (K_1/K_2) = 1.27$; $\log K_1 = 8.23$; $\log (K_1K_2) = 15.19$; $\sigma = \pm 0.007$

pA	8.421	8.240	8.054	7.850	7.610	7.230	7.100	6.980	6.830
$\bar{n}_{exp.}$	0.423	0.547	0.663	0.818	0.989	1.260	1.356	1.450	1.550
$\Delta\bar{n}$	−0.0085	−0.013	+0.003	−0.003	+0.011	+0.007	+0.006	−0.003	−0.001

30°; $\log (K_1/K_2) = 1.28$; $\log K_1 = 8.17$; $\log (K_1K_2) = 15.06$; $\sigma = \pm 0.007$

pA	8.350	8.180	7.990	7.780	7.550	7.420	7.160	7.040	6.910
$\bar{n}_{exp.}$	0.433	0.540	0.671	0.821	0.991	1.080	1.265	1.360	1.440
$\Delta\bar{n}$	−0.013	−0.009	−0.005	−0.003	−0.006	−0·000	+0.005	−0.004	+0.008

Calculation of enthalpy and entropy changes

From Tables V and VI it is also obvious that in the temperature range studied the change of the constants is nearly linear. In view of this it is possible to calculate the enthalpy changes of the processes, with the temperature coefficient method, by means of the equation:

$$\Delta H = \frac{2.303\, RTT' (\log K' - \log K)}{T' - T}, \tag{15}$$

while the entropy changes of the complex-forming processes are calculated on basis of the relation:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{16}$$

The results are shown, together with some corresponding values reported in the literature, in Table VII.

From the data summarized in Table VII, the most accurate are those of BRANNAN *et al.* and IZATT *et al.* The data of LI *et al.*, improbably high for enthalpy changes, and very small or negative for entropy changes, have already been criticized in IZATT's paper mentioned above.

In can be seen from Table VII that our results are, in spite of the difference in ionic strength, in very good agreement with those of BRANNAN *et al.*

Table VII

ΔH and ΔS values of the systems Ni(II)-glycine and Cu(II)-glycine

Metal ion	Method	I	$-\Delta H_1$ kcal/mole	$-\Delta H_2$ kcal/mole	ΔS_1 e. u.	ΔS_2 e. u.
Ni (II)	hydrogen[a] electrode	0	4.09	4.69	14.5	6.9
	glass[b] electrode	0.2	8.8		20	
	polarograph:[c]	0.15	14		2.5	
	glass[d] electrode	0.1	4.1	5.3	13	4
Cu (II)	calorimetric[e]	0	6.0	6.4	19	11
	glass[f] electrode	0.02	7.0	—	13	—
	glass[b] electrode	0.2	10.7		34	
	polarograph:[c]	0.15	21		—1	
	glass[d] electrode	0.1	5.9	6.5	18	11

a) I. R. BRANNAN, H. S. DUNSMORE, G. H. NANCOLLAS: J. Chem. Soc. **1964,** 304.
b) V. S. SHARMA, H. B. MATHUR, A. B. BISWAS: J. Inorg. Nucl. Chem. **26,** 382 (1964).
c) N. C. LI, I. W. WHITE, R. L. YOEST: J. Am. Chem. Soc. **78,** 5218 (1956).
d) Present work
e) R. M. IZATT, I. I. CHRISTENSEN, V. KOTHARI: Inorg. Chem. **3,** 1565 (1964).
f) C. B. MURPHY, A. E. MATELL: J. Biol. Chem. **226,** 37 (1957).

and IZATT *et al.* The maximum difference in enthalpy changes is 0.6 kcal/mole. The values of entropy changes agree also well with the data of the above-mentioned authors. Consequently, it is evident that the calculated stability constants, too, are sufficiently accurate. This is due to the accuracy of pH measurements, as well as to that of the calculation method developed by us. However, it should be emphasized once again that in favourable cases (at suitable values of log (K_1/K_2) and if we have a nearly complete and accurate formation curve at our disposal) the desired accuracy can be achieved with the correction term and projection strip calculation methods as well.

The authors are indebted to Prof. PÁL SZARVAS for his valuable advice and help in this research. Thanks are due to Mrs. MARIA NAGYPÁL-TÓTH for her assistance in the experimental work.

SUMMARY

A new method for the calculation of stability constants has been developed. The procedure starts with the assumption that the size of the area determined by two points of the formation curve, depends apart from $\bar{n}$, only on the ratio of the stability constants. Accordingly, in the case of a known area determined by graphic integration, the values for log (K_1/K_2) can be obtained. From this latter the correction term (y) necessary to compute the stability constants can be determined either through calculation or graphically. For nineteen points of the formation curve, changing the value of log (K_1/K_2) from 0 to 4 by intervals of 0.2, we have calculated and tabulated the corresponding area-values.

Our procedure is essentially a modification of the correction term method. It can be employed for the calculation of log K_1 and K_2 in the case of $N = 2$ and $N = 3$, too. The utilizability of the calculation method has been proved for the systems Ni(II)-glycine and Cu(II)-glycine. By means of the stability constants obtained at various temperatures, with the temperature coefficient method, we have calculated the enthalpy and entropy changes corresponding to the above complex-forming processes. These values for Cu(II)-glycine are as follows: $\Delta H_1 = 5.9$ kcal/mole; $\Delta H_2 = 6.5$ kcal/mole; $\Delta S_1 = 18$ e. u.; $\Delta S_2 = 11$ e. u.; and for Ni(II)-glycine: $\Delta H_1 = 4.1$ kcal/mole; $\Delta H_2 = 5.3$ kcal/mole; $\Delta S_1 = 13$ e. u.; $\Delta S_2 = 4$ e. u. The enthalpy changes, within ± 1 kcal/mole are in good agreement with the data reported in the literature, obtained calorimetrically.

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SELECTIVE QUATERNIZATION OF COMPOUNDS WITH MORPHINE SKELETON

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It has been reported earlier [1] that high stereoselectivity could be observed in the quaternization of codeine with benzyl iodide and in the reaction of N-benzyl-norcodeine with methyl iodide; these reactions afforded quaternary ammonium salts stereoisomeric at the nitrogen atom, having essentially different physical properties. Our researches into the selectivity of "direct" and "reverse" quaternization were extended to include 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives [2], and related compounds such as laudanosine homologues [3] and other 1,2-disubstituted 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives [4]. Similar investigations are also known on other models, such as N-alkyl-camphidine derivatives [5], *orto* substituted dimethylaniline [6], 5-nitro-tetrahydrooxazines [7], indolizidine compounds [8], 2-methylpyrrolidine, 2-methyl- and 4-phenylpiperidine, *trans*-decahydroquinoline [9a], N-methyl-4-aza-5α-cholestane [9b], etc. Attempts have been made to determine the orientation and relative spatial requirement of the unshared pair of electrons of the tertiary nitrogen atom by quantum mechanical calculations and by physico-chemical methods [10], and several other aspects of this field of research are the subject of discussion [11].

In 1961 we reported first on our investigations directed to the quaternization of morphine* (**I**) and N-allyl-normorphine (**II**) [12]. We found that both the quaternization of morphine (**I**) with allyl iodide and the reaction of N-allyl-normorphine (**II**) with methyl iodide led in fair yields to quaternary ammonium salts (**III**) and (**IV**) which were stereoisomeric at the nitrogen atom and had different physical properties. However, even the preparative technique and evaluation applied at that time revealed that N-allyl-normorphine methiodide (**IV**), being the main product of the quaternization of N-allyl-normorphine with methyl iodide, was accompanied by a small amount of the N-stereoisomeric compound, morphine-N-allyl iodide (**III**); the latter could be isolated from the mother liquor of the crystallized main product (Fig. 1).

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* Several ways are known [14, 18] to represent the cyclohexene ring of the morphine skeleton. Experimental decision as regards the correct form has not been possible so far. Since this paper, we use here the latest mode of representation [15].

In later experiments, in the quaternization of morphine (**I**) with allyl iodide, we succeeded in isolating during the preparative processing of the reaction mixture, besides morphine-N-allyl iodide (**III**) formed as the main product, also the stereoisomeric compound, N-allyl-normorphine methiodide (**IV**) (Fig. 2).

It may be mentioned in this connection that earlier, on the basis of results obtained by independent researches, the quaternization reactions of a number of tropane derivatives had been considered completely selective [13]. In 1965 McKenna concluded from a proton resonance spectroscopical investigation that the quaternization of compounds with tropane skeleton was selective to a great extent, but not completely so.

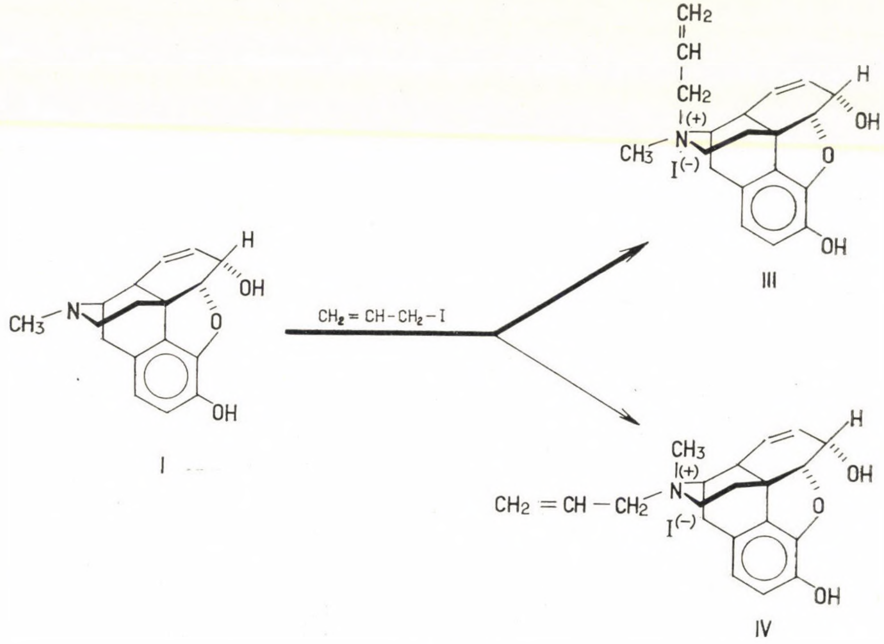

Fig. 1

An examination by preparative methods of the quaternization of codeine during our earlier experiments showed that the product was homogeneous [1]. In fact, quaternization reactions in the morphine series afford in several instances nearly homogeneous products from the preparative point of view. The quaternary salt stereoisomeric at the nitrogen atom formed along with the main product quaternary salt can be isolated as a pure compound only by careful fractional crystallization. This is also shown by the fact that up to our investigations, the simultaneous formation of N-stereoisomeric compounds has not been reported in any quaternization in the morphine series, though it should be noted that the purposes of the related experiments were other than stereochemical research. The first pair of salts stereoisomeric at the nitrogen atom and having morphine skeleton described in literature was actually codeine-N-benzyl iodide (**V**) and N-benzyl-nor-codeine methiodide (**VI**) prepared by us by two different routes.

The high selectivity of quaternization reactions in the morphine series is also indicated by the work of Bognár and Szabó [15] who studied the quaternization of O_3,O_6-diacetylmorphine with allyl bromide, and of O_3,O_6-diacetyl-N-allyl-normorphine with methyl bromide, further of O_3,O_6-diacetylmorphine with *n*-propyl bromide and of O_3,O_6-diacetyl-N-*n*-propyl-normorphine with methyl bromide. In the reactions conducted at room temperature, complete selectivity was experienced; the formation of any by-product in the quaternization reactions was not noted.

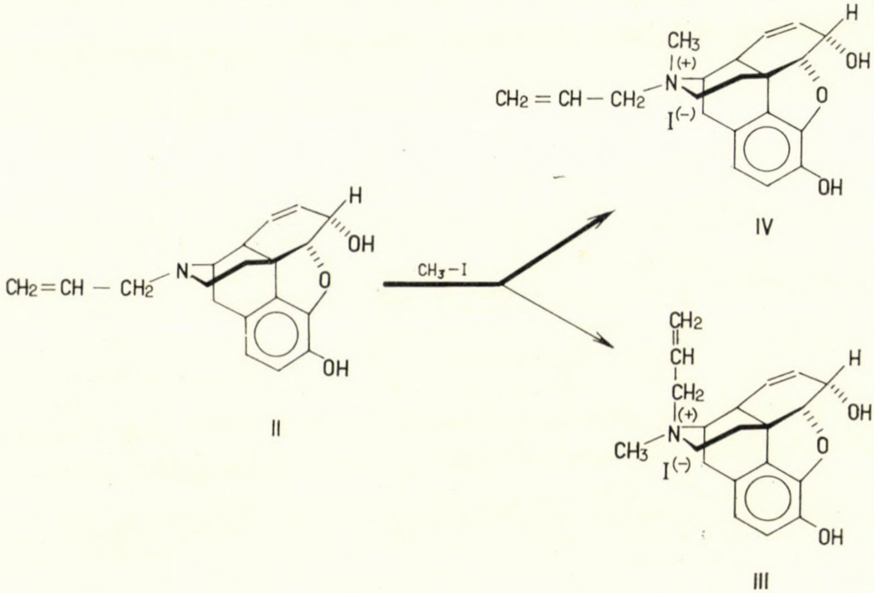

Fig. 2

In addition to the preparative methods used in the beginning, the selectivity of the quaternization reactions of morphine and N-allyl-normorphine was evaluated later also by infrared spectroscopy. Here we utilized the fact that essential differences exist in the infrared spectra of the stereoisomeric quaternary ammonium salts [13c, 5, 9a]. Evaluation by NMR spectroscopy was in this case impossible, owing to the poor solubility of the compounds in the solvents normally used for an NMR study.

Differences in the infrared spectra of morphine-N-allyl iodide (**III**) and N-allyl-normorphine methiodide (**IV**) made possible, in addition to the detection of minute amounts of isomeric contaminants in this way, also the determination of the steric orientation of the substituents in quaternary salts, outside the ring, coupled to the nitrogen atom, utilizing known regularities in this work. Also the isomerization of quaternary salts could be well evaluated by infrared spectroscopy. The results furnished further information about the conformation of these compounds.

A detailed discussion of the infrared spectra, compared with the infrared and NMR spectra of a number other salts, nor-compounds and quaternary derivatives of morphine skeleton, of N-stereoisomeric 1,2,3,4-tetrahydroisoquinolinium salts and quaternary 1,2,3,4-tetrahydroisoquinoline derivatives. will be published later. In the present paper we discuss only the difference used in the evaluation of the reactions and for establishing the conformationss

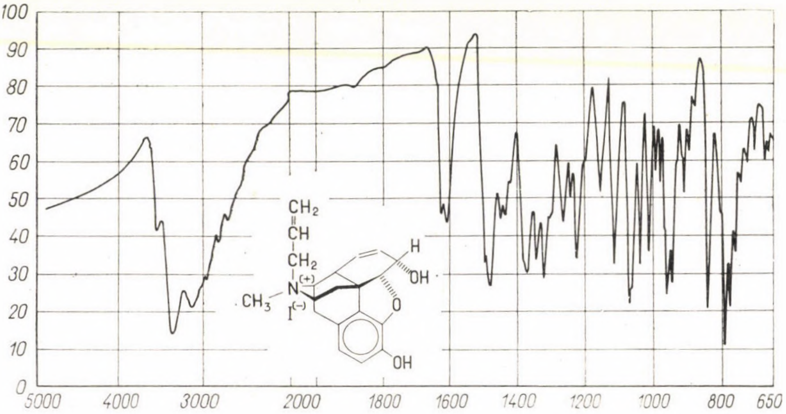

Fig. 3

The infrared spectra of morphine-N-allyl iodide (**III**) and of N-allyl-normorphine methiodide (**IV**) significantly differ from each other in the spectra range of 1610—1637 cm^{-1} of the aromatic C—C bands. In the spectrum of morphine-N-allyl iodide (Fig. 3) the bands of the doublet at 1628 and 1610 cm^{-1} show nearly the same intensity, while in the spectrum of N-allyl-normorphine methiodide (Fig. 4) the doublet is found at 1630 and 1610 cm^{-1}, and the band at 1630 cm^{-1} has only half the intensity of the band at 1610 cm^{-1}.

The strong doublet at 1080—1096 cm^{-1} in the spectrum of N-allyl-normorphine methiodide (**IV**) is very characteristic. In the spectrum of morphine-N-allyl iodide, in turn, the band at 1096 cm^{-1} is completely absent, and strong absorption is seen only in the vicinity, at 1074 and 1118 cm^{-1}. The absorption band of morphine-N-allyl iodide appearing at 1016 cm^{-1} is split into the doublet 1010 and 1031 cm^{-1}. A very characteristic difference is that in the spectrum of morphine-N-allyl iodide there is an extremely strong sharp singlet at 842

cm^{-1}, while in the spectrum of N-allyl-normorphine methiodide in the same range a doublet is found at 850 and 862 cm^{-1}.

There is another significant difference in the range of 1460—1510 cm^{-1} of the spectra. In the spectrum of N-allyl-normorphine methiodide a band of high intensity is present. This band is absent in the spectrum of morphine-N-allyl iodide where absorption is observed at 1482 cm^{-1}. From this fact, taking into account the observation of ZEILE and SCHULZ [13c] according to which an absorption band appears at 1482 cm^{-1} in the spectra of the methiodides of the N-alkyl-nortropane derivatives carrying the N-methyl group in *equatorial* position, while in the spectra of tropane alkyl quaternary compounds carrying the N-methyl group in *axial* position only a shoulder appears at about the same wave number, it may be concluded that in morphine-N-allyl iodide (**III**) the N-methyl group occupies *equatorial* position, though the analogy is not too close.

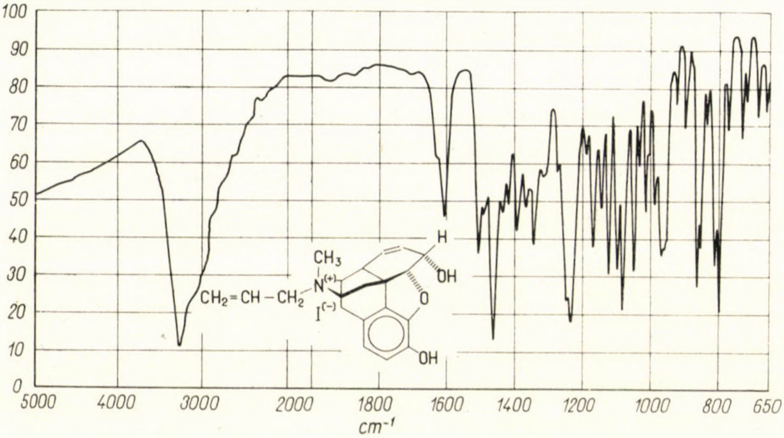

Fig. 4

Our above-mentioned conclusion based on the infrared spectra has also been supported by the evaluation of the selectivities of quaternization reactions and by the isomerization of quaternary salts. These reactions were carried out in chloroform, methanol, ethanol and benzene at +4 °C, or at room temperature, or at the boiling point of the solution. Besides preparative processing, also the infrared spectrum of the homogenized crystalline residue obtained on evaporating the reaction mixture was investigated. Highest selectivity was observed in the reaction of N-allyl-normorphine with methyl iodide in chloroform at +4 °C. In that case the amount of morphine-N-allyl iodide (**III**) formed as the by-product was about 15%. The quaternization of morphine (**I**) with allyl iodide showed a lower degree of selectivity. On raising the temperature, the selectivities of both reactions slightly decreased. It has been found that the selectivity of quaternization reactions in chloroform is higher than in methanol or ethanol.

The racemization of optically active quaternary ammonium salts containing an allyl radical has been studied by WEDEKIND [16]. The isomerization in chloroform of inactive stereoisomeric quaternary salts containing a benzyl radical has recently been utilized by MCKENNA [9c] to establish the conformation of alicyclic quaternary salts. On heating morphine-N-allyl iodide (**III**) in a sealed tube in chloroform at 80° for 80 to 100 hours, partial isomerization to N-allyl-normorphine methiodide (**IV**) took place (Fig. 5). In contrast to that, N-allyl-normorphine methiodide (**IV**) suffered only negligible change under identical conditions.

On subjecting codeine-N-benzyl iodide (**V**) to isomerization under similar conditions, the formation of N-benzyl-norcodeine methiodide (**VI**) was observed (Fig. 6). The latter conversion took place also on melting codeine-N-benzyl iodide in a sealed tube, to the analogy of the observations of SCHOLTZ [17] with the benzyl quaternary derivatives of coniine and conhydrine. On heating N-benzyl-norcodeine methiodide (**VI**) in chloroform, only slight isomerization was experienced. The assay by infrared spectroscopy employed to evaluate the selectivity of quaternization and of the isomerization of quaternary salts, has been well complemented by the measurement of the optical rotatory powers of the crude reaction products or of the substance obtained on isomerization. Since the optical rotatory activities of morphine-N-allyl iodide and N-allyl-normorphine methiodide differ considerably, the values of rotatory power of the crude products of quaternization furnished also an approximately quantitative result as regards the selectivity of the reactions. These data were in accordance with the selectivity values obtained on the basis of the infrared spectra.

Similarly, it was a convincing piece of evidence that while practically no decrease of the optical rotatory power of morphine-N-allyl iodide was perceptible during isomerization for 80—100 hours at 80° in chloroformic solution (the decrease of rotatory power corresponded to the formation of 5% of morphine-N-allyl iodide only) after similar treatment of the isomeric N-allyl-normorphine methiodide the optical rotatory power of the end product significantly exceeded that of the initial substance. The observed rise of the rotatory power corresponded to the formation of about 20—25% of N-allyl-normorphine methiodide.

From the above-discussed facts it can be unequivocally concluded that in the course of the investigated quaternization reactions in the morphine series, the substituent coupled to the nitrogen atom in the second instance occupies *axial* steric position in the quaternary salt formed as the main product. Consequently, in the quaternary salts formed as main products in the quaternization of morphine, the spatial position of the N-methyl group coupled

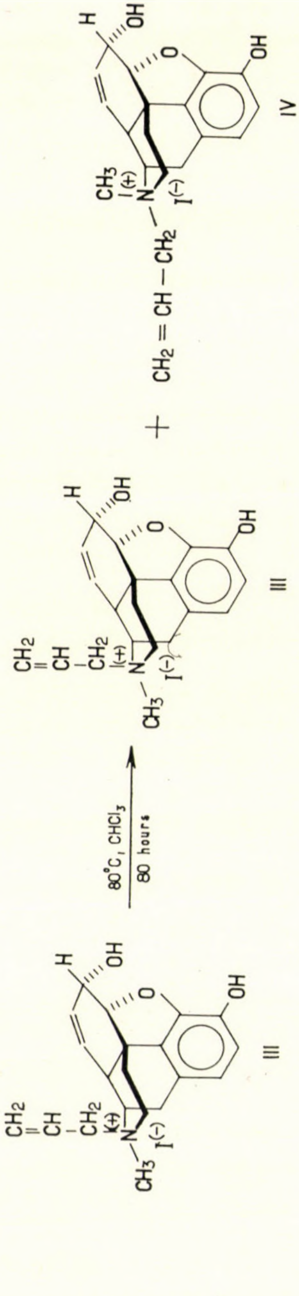
CH2=CH–CH2
CH3
N
(+)
I(−)
H
OH
O
OH
III
80°C, CHCl3
80 hours
III
+
CH2 = CH – CH2
CH3
IV

Fig. 5.

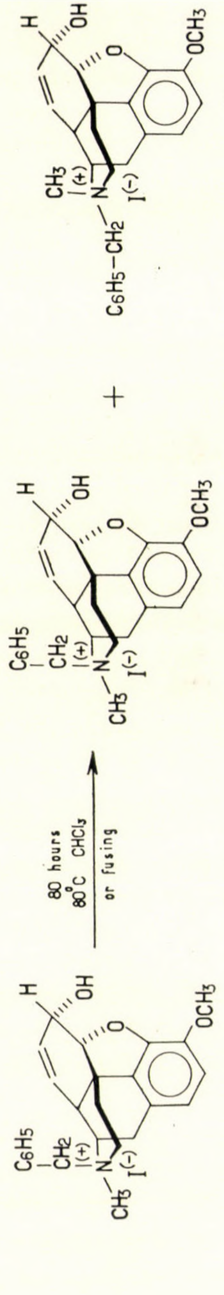
C6H5–CH2
CH3
N
(+)
I(−)
H
OH
O
OCH3
V
80 hours
80°C CHCl3
or fusing
V
+
C6H5–CH2
CH3
VI

Fig. 6.

to nitrogen atom is the same as that determined in crystalline codeine. HI.$2H_2O$ by X-ray diffraction method [18]. Thus, the formulas applied earlier correctly express the configuration of the stereoisomeric quaternary salts with morphine skeleton.

A comparative evaluation of the optical rotatory power of the hydrogen halides of nor-compounds and tertiary and quaternary derivatives afforded [19] a further, independent evidence to support our statement concerning the configuration of quaternary salts with morphine skeleton.

Experimental

Melting points were determined according to the capillary tube method, unless stated otherwise, and are uncorrected.

Morphine-N-allyl iodide (III)

5.0 g (0.0175 mole) of morphine (**I**) in 65 ml of methanol was allowed to stand two weeks at room temperature with 4.0 g (0.022 mole) of allyl iodide. Lentil-shaped hard crystals (5.85 g; 70.8%) precipitated (fraction 1) m. p. 229—230° (decomp.). On basis of the infrared spectrum, the substance consisted mainly of morphine-N-allyl iodide (**III**) containing about 10—15% of N-allyl-normorphine methiodide (**IV**) formed as by-product. In the spectrum of this crude product, besides the other lines of N-allyl-normorphine methiodide, the isolated band at 1096 cm^{-1} is particularly characteristic, together with the shift towards higher wave numbers and the broadening of the strong sharp singlets of the very characteristic band of morphine-N-allyl iodide (**III**) seen at 842 cm^{-1}. This latter band is due to the similarly characteristic doublet which is found at 850 and 862 cm^{-1} in the spectrum of N-allyl-normorphine methiodide (**IV**) present as contaminant. Five recrystallizations from water gave 2.6 g of well developed needles of m.p. 241—242° (decomp.). The infrared spectrum showed that this substance did not contain any N-allyl-normorphine methiodide. The m. p. measured in a Kofler apparatus was lower: 230—231°. The loss of the water of crystallization was observed in the temperature range 140—160°. On prolonged drying, the water of crystallization was eliminated at lower temperatures. $C_{20}H_{24}NO_3I.H_2O$ (471.33). Calcd. C 50.96; H 5.56; I^- 26.93; H_2O 3.82. Found C 50.73; H 5.63; I^- 27.08; H_2O 4.02%.

After drying 3 hrs. at 117° and 25 Torr, we had: $C_{20}H_{24}NO_3I$ (453.33) Calcd. C 52.99; H 5.34. Found C 53.17; H 5.50%. $[\alpha]_D^{23} = 45.7°$ (c = 0.201, in water).

Evaporation of the mother liquor of fraction 1 gave 0.7 g (8.5%) of a substance of m.p. 225—227° in which the infrared spectrum showed enrichment of N-allyl-normorphine methiodide (**IV**). Further processing of the mother liquor yielded 0.9 g (10.9%) of a substance consisting mainly of morphine-N-allyl iodide (**III**) the total yield being thus 7.45 g (90.2%).

N-allyl-normorphine methiodide (IV)

(a) 3.0 g (0.0096 mole) of N-allyl-normorphine (**II**) in 30 ml of methanol was refluxed 3 hrs. with 3.0 g (0.021 mole) of methyl iodide, then the reaction mixture evaporated to dryness, and the residue crystallized from 90% methanol to obtain 3.4 g (75.1%) of platelet crystals (fraction 1), m.p. 246° (decomp.) On the basis of the infrared spectrum, this product was nearly completely homogeneous N-allyl-normorphinemethiodide (**IV**). Three recrystallizations from 90% methanol gave plates of m.p. 255—256°. According to the infrared spectrum, the substance did not contain any of the N-stereoisomeric compound (**III**).
$C_{20}H_{24}NO_3I.H_2O$ (471.33). Calcd. C 50.96; H 5.56; H_2O 3.82. Found C 51.03; H 5.83; H_2O 3.83%.

On drying the substance at 117° and 25 Torr, it decomposed to a crystalline powder.
$C_{20}H_{24}NO_3I$ (453.33). Calcd. C 52.99; H 5.34. Found C 53.11; H 5.29%. $[\alpha]_D^{23} = 110.2°$ (c = 0.203; in water).

On drying the substance under an infrared lamp at 60—80°, it loses the water of crystallization within 1—2 hrs. Meanwhile, the platelet crystals decompose to a crystalline powder. Morphine-N-allyl iodide (**III**) which crystallized from water in needles containing similarly one molecule water of crystallization, lost this water less readily.

Evaporation of the mother liquor of fraction 1, and crystallization of the residue from water gave 0.8 g (17.6%) of a crystalline powder, m.p. 224—226°. Repeated recrystallizations from water yielded 0.4 g of needles, m.p. 237—239° (decomp.), which showed no depression in mixed m.p. determination with morphine-N-allyl iodide.H_2O. According to the infrared spectrum, the product was homogeneous morphine-N-allyl iodide. Total yield: 4.2 g (92.7%).

(b) 1.2 g (0.0038 mole) of N-allyl-normorphine (**II**) in 25 ml of anhydrous methanol was allowed to stand two weeks at room temperature with 1.0 g (0.007 mole) of methyl iodide. On cooling the mixture, 1.5 g (75.7%) of glossy prisms separated (fraction 1), m. p. 256—257° (decomp.). The infrared spectrum showed the substance to be nearly homogeneous N-allyl-normorphine methiodide (**IV**) containing less than 10% of morphine-N-allyl iodide (**III**). Recrystallization from anhydrous methanol gave m.p. 261—262°. The melting point and infrared spectrum remained unchanged on repeated recrystallization.
$C_{20}H_{24}NO_3I$ (453.33).Calcd. C 52.99; H 5.34. Found C 52.82; H 5.67%.

Evaporation of the mother liquor of fraction 1 to about 5 ml and cooling yielded 0.3 g (15.1%) of a crystalline powder of m.p. 227—230°, which according to the infrared spectrum consisted mainly of morphine-N-allyl iodide (**III**). By evaporating the mother liquor further, 0.14 g (7.1%) of an approximately 1 : 1 mixture of morphine-N-allyl iodide (**III**) and N-allyl-normorphine methiodide (**IV**) was obtained.

Study of the quaternization reaction of morphine (I) and N-allyl-normorphine (II), based on evaluation by infrared spectroscopy

200 mg of morphine (**I**) and 0.2 ml of allyl iodide, or 200 mg of N-allyl-normorphine (**II**) and 0.2 ml of methyl iodide were allowed to stand with 20 ml of methanol, ethanol, benzene, or chloroform at +4 °C, at room temperature for 8 to 10 days, or refluxed for 3 to 6 hrs. The reaction mixture was then evaporated at a temperature lower than that of the quaternization, and the homogenized crystalline residue examined by infrared spectroscopy. The infrared spectra were recorded with pellets made of 3 mg of substance and 300 mg of KBr, using a *Zeiss UR* 10 or a *Unicam SP* 200 infrared spectrophotometer. The differences appearing in the ranges 1610—1637 cm^{-1} and 1080—1096 cm^{-1} were employed for evaluation, taking into account, as a completion, also the spectral lines 1010—1031 and 842—862 cm^{-1}. Highest stereospecificity (less than 15% of isomeric by-product) was observed in the reactions of N-allyl-normorphine with methyl iodide at +4° in chloroform, or in benzene at room temperature. In methanol or ethanol the selectivity of the quaternization reaction was lower; when these reactions were carried out at the boiling point of the solutions, the reaction product usually contained 15—25% of the isomeric by-product quaternary salt. In the quaternization of morphine with allyl iodide, selectivity was lower than in the reaction of N-allyl-normorphine with methyl iodide.

Isomerization experiments

(a) 200 mg of morphine-N-allyl iodide in 120 ml of anhydrous chloroform was heated in a sealed tube for 80 hrs. at 80 ±2°. The homogenized crystalline substance obtained on evaporation was subjected to infrared analysis as described above. The spectrum unequivocally proved that part of the initial morphine-N-allyl iodide (**III**) had been isomerized to N-allyl-normorphine methiodide (**IV**).

(b) 200 mg of N-allyl-normorphine methiodide (**IV**) in 120 ml of anhydrous chloroform was kept 80 hrs. at 80 ±2° in a sealed tube. After processing the product as described under *(a)*, the spectrum did not show any change indicating the formation of morphine-N-allyl iodide (**III**).

(c) 200 mg of codeine-N-benzyl iodide (**V**) in 120 ml of anhydrous chloroform was kept in a sealed tube 80 hrs. at 80 ±2°. Isomerization was evaluated as described above. In the ranges 800—1000 cm^{-1} and 1100—1200 cm^{-1}, the bands characteristic of N-benzyl-norcodeine methiodide (**VI**) became more intensive. The increase of intensity was particularly pronounced with the band at 1958 cm^{-1}. The band at 1395 cm^{-1} appeared in a merged form.

(d) 200 mg of codeine-N-benzyl iodide (**V**) was kept 5 and 20 minutes, respectively, in a sealed tube at 195 ±2°. The melted and solidified substance was homogenized after cooling, and its infrared spectrum was obtained as described above. From the changes in band intensities observed in the ranges mentioned under *(c)*, it unequivocally followed that codeine-N-benzyl iodide (**V**) had been isomerized to N-benzyl-norcodeine methiodide (**VI**). In addition to the intensity increase of the band at 1958 cm^{-1}, the changes in the spectral range 2800—3050 cm^{-1} are also characteristic in this case.

Some decomposition could be concluded from both the spectra and the slight benzyl iodide smell of the solidified melt, however, the yellow colour of the product was very slight even after melting for 20 minutes.

(e) 200 mg of N-benzyl-norcodeine methiodide (**VI**) was processed as described under *(c)*. Though there was some difference between the IR spectra of the starting material and end product, no conversion into codeine-N-benzyl iodide (**V**) could be concluded unequivocally.

Thanks are expressed to Professor K. Kovács, head of the Institute for his constant interest and advice during this work. Thanks are due to Mr. J. A. Szabó for recording the infrared spectra, and to Mrs. K. Lakos-Láng and Mrs. G. Bartók-Bozóki for the microanalyses.

SUMMARY

The quaternization reactions of morphine (**I**) with allyl iodide and of N-allyl-normorphine (**II**) with methyl iodide have been studied by preparative methods and by evaluation based on infrared spectroscopy. Isolation of the produced quaternary salts, and examination of the isolated fractions and crude reaction products by infrared analysis have shown that besides the quaternary derivative (**III** and **IV**, respectively) obtained in both reactions as the main product, also the quaternary compound stereoisomeric at the nitrogen atom (**IV** and **III**, respectively) is formed. Heating of morphine-N-allyl iodide (**III**) and of codeine-N-benzyl iodide (**V**) in chloroform gives rise to partial isomerization into N-allyl-normorphine methiodide (**IV**) and N-benzyl-norcodeine methiodide (**VI**), respectively. The relative selectivities of the quaternization reactions, further the infrared spectra and the isomerization of the quaternary salts indicate that the substituent introduced during quaternization occupies *axial* position in the quaternary salt obtained as the main product.

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CHEMICAL TRANSFORMATIONS OF DIOLS AND CYCLIC ETHERS, XIX*

STUDY OF THE THERMAL DEGRADATION OF 2-MONOSUBSTITUTED OXETANES BY THE MICROREACTOR TECHNIQUE

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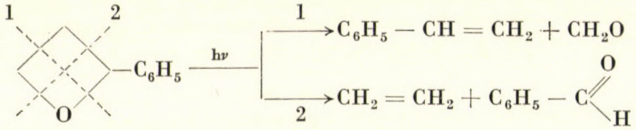
Received May 2, 1966

Our studies of the chemistry of cyclic ethers have included an investigation of the reactions of these compounds, on thermal treatment with the aim to gain information on the stability of cyclic ethers and on the course and rate of their thermal degradation. The present paper reports on recent results concerning the thermal decomposition of 2-monosubstituted oxetanes.

Apart from our earlier communications [1, 2], the thermal degradation of 2-monosubstituted oxetanes has not been dealt with in the literature. Margerum *et al.* [3] describe the photocatalyzed degradation of 2-phenyloxetanes; this work has some bearing on our researches since it allows a comparison of the photocatalytic reactions with the experimental results of the thermolysis of oxetanes. According to the above authors, the primary degradation of 2-phenyltrimethylene oxide proceeds in the following way:



The ratio between Reactions 1 and 2 is 3.5 : 1. The main processes are accompanied by several secondary reactions.

In the experiments described in this paper, the thermal decomposition reactions of 2-methyl-, 2-*n*-propyl-, 2-isopropyl-, 2-*n*-butyl-, 2-cyclohexyl- and 2-phenyloxetanes were studied. Under experimental conditions analogous to those applied for 3-monosubstituted oxetanes [4, 5,] in a continuous system by the microreactor technique, between 300° and 500 °C. The 2-monosubstituted oxetanes were prepared by the methods described previously [6]. The temperature dependence of the thermolysis reactions is shown in Fig. 1.

Degradation starts at a relatively low temperature, and it is practically complete at 500—520°. 2-*n*-Propyloxetane decomposes at the relatively highest rate; the decomposition of 2-isopropyloxetane is the slowest. This experi-

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* Part XVIII: Izv. A. N. USSR, Ser. Khim. (In the press).

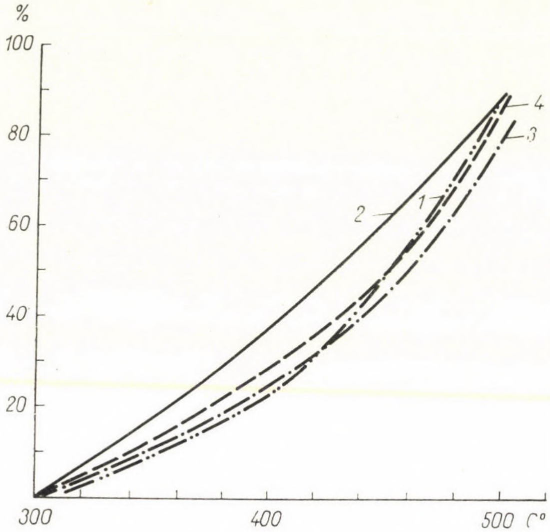


Fig. 1
1. 2-Methyloxetane
2. 2-*n*-Propyloxetane
3. 2-Isopropyloxetane
4. 2-*n*-Butyloxetane

mental fact may be explained by the position of the isopropyl group in the BAKER—NATHAN sequence (*cf.* [5]).

The direction of thermal degradation was established by an examination of the degradation chromatograms. Figs 2—7 show the characteristic chromatograms of the thermal decompositions of 2-monosubstituted oxetanes where the peaks correspond to the following substances:

> 1 carbon monoxide, 2 olefin formed in Reaction 1, 3 aldehyde isomeric with the oxetane, 4 the corresponding oxetane derivative, 5 α, β-unsaturated alcohol isomeric with the oxetane.

In the chromatograms the following denotations are used: *1* the quantity (in ml) of 0.2—0.4 mm particle size quartz (Q) microreactor packing and its temperature in °C; *2* length (in m) of the chromatographic column of 5 mm internal diameter, and the quality of the packing: 15% apiezon "L" grease (A), or silicone grease on 0.2—0.4 mm particle size thermolite or aluminium oxide (Al_2O_3); *3* temperature of the thermostat of the chromatograph; *4* flow rate of the helium (He) carrier gas; *5* detector current in mA; *6* sensitivity of the Willy Giede Type GCHF 18/2 gas chromatograph (1/2 = final deflection of the compensograph, 4 mV); *7* quantity of substance injected into the microreactor (in ml).

Chromatograms of the products formed in the thermal degradation of 2-methyloxetane

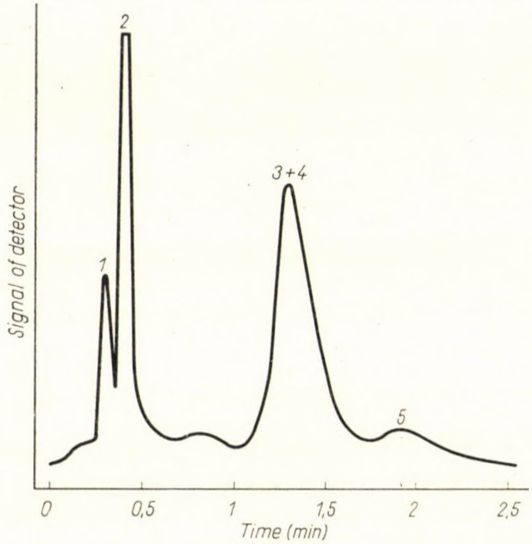


Fig. 2
1. 1.1 Q, 450; 2. 1 A; 3. 140; 4. 50 He; 5. 140; 6. 1/2; 7. 0.005

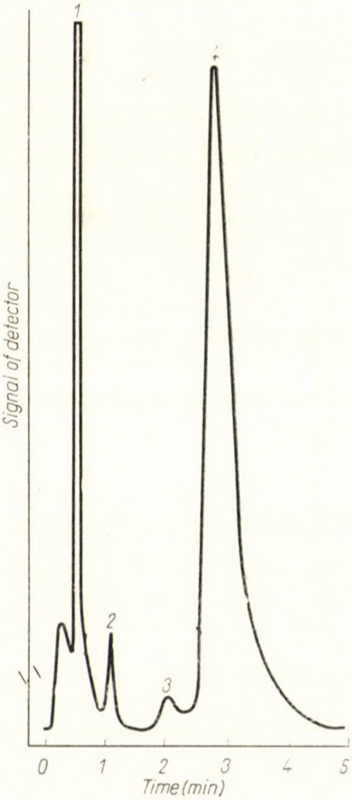
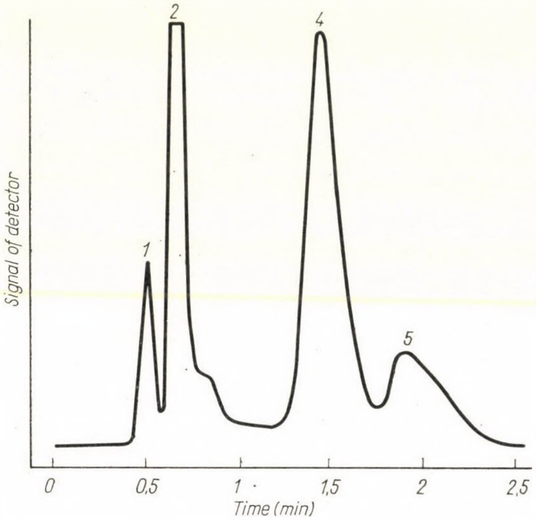
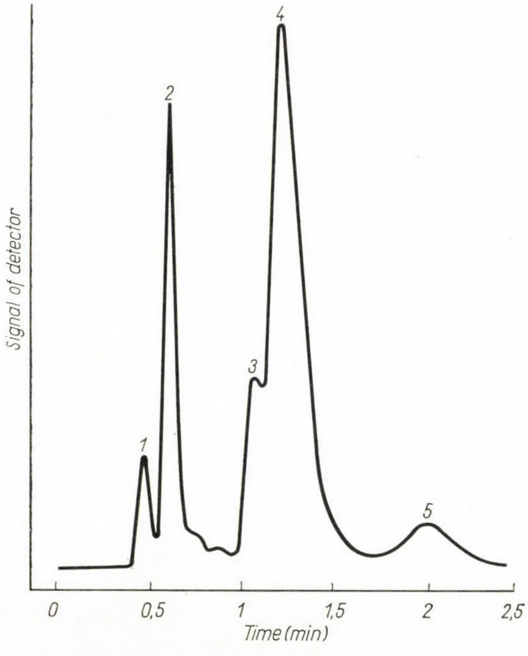


Fig. 3
1. 1.1 Q, 500; 2. 1 Al_2O_3; 3. 80; 4. 50 He ; 5. 140; 6.1/2; 7. 0.01

The peaks represent: 1 CO, 2 ethylene, 3 propane, 4 propylene.

Chromatograms of the products formed by the thermal degradation of 2-n-propyl- and 2-isopropyloxetanes





Figs 4 and 5

1. 1,1 Q, 450; 2. 1 silicone grease; 3. 160; 4. 50 He; 5. 240; 6. 1/8; 7. 0,01.

Chromatograms of the products formed by the thermal degradation of 2-n-butyl- and 2-cyclohexyloxetanes

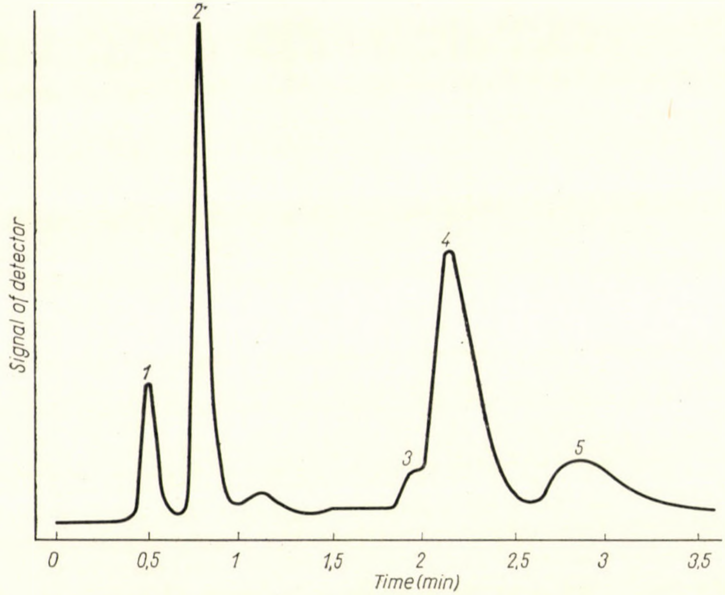


Fig. 6

1\. 1.1 Q; 450; 2. 1 silicone grease; 3. 160; 4. 50 He; 5. 140; 6. 1/8; 7. 0.01

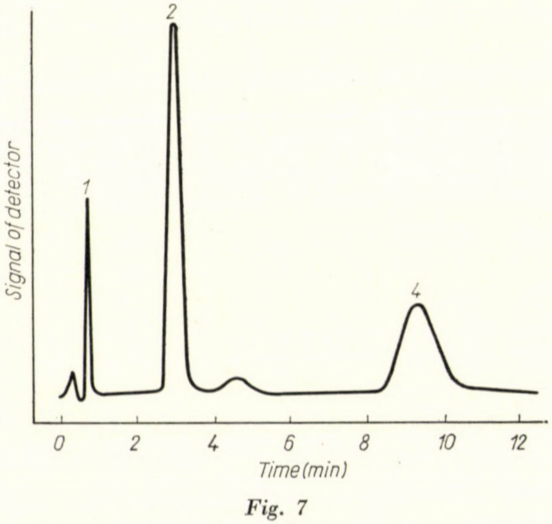
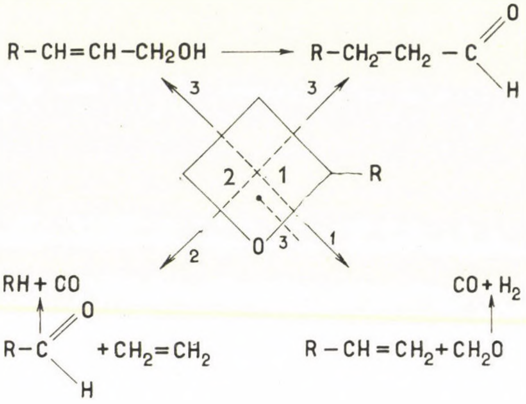


Fig. 7

1\. 1.1 Q, 450; 2. 1 A; 3. 200; 4. 50 He; 5. 140; 6. 1/2; 7. 0.01

According to the above results, the thermal degradation of 2-monosubstituted oxetanes may be represented as follows:



where R stands for a methyl, *n*-propyl, isopropyl, *n*-butyl, cyclohexyl or phenyl group.

A quantitative evaluation of the thermolysis of 2-monosubstituted oxetanes shows that Reaction 1 takes place in 80—90%. Thus the main process is a transformation starting with the splitting of the C—O bond neighbouring the substituent and resulting in the formation of an alkene-1 and formaldehyde. The second direction of degradation is negligible (Fig. 3, peak 2) and is entirely absent in the case of 2-phenyltrimethylene oxide. The isomerization processes (Reactions 3) are probably due to wall effects. Thermal degradation is accompanied by the secondary process of decarbonylation of the aldehydes.

Experimental

The microreactor technique, *i. e.* a microreactor attached to a *Willy Giede GCHF 18 2* gas chromatograph was used for the study of the thermal degradation of oxetanes. The method has been described in detail in our earlier communications [7, 8].

Several variants of the microreactor technique are known from the literature. For the study of the thermal degradation of oxetanes the simple "impulse" input was applied. According to this method 0.005 to 0.01 ml of the substance under investigation was introduced into the carrier gas before the reactor. The carrier gas rinsed the products of thermolysis directly into the separating column of the gas chromatograph. Helium was used as the carrier gas. The microreactor was heated with 24 V 20 A a. c. by means of a *Kanthal* filament wound on the reactor. This low voltage high intensity current made possible to change the temperature of the reaction zone very rapidly. Temperature was controlled by a photoresistance temperature control system and measured with an iron-constantan thermocouple. The reaction space was filled with quartz chippings of 0.2—0.4 mm particle size.

The processes taking place were evaluated by the quantitative and qualitative analysis of the chromatograms. The complex nature of the products to be analyzed (saturated and unsaturated hydrocarbons in the gaseous and liquid phase, isomeric carbonyl compounds and oxetanes, *etc.)* necessitated trials with several adsorbents and stationary phases. Columns packed with aluminium oxide were found to be the best for the separation of gaseous products, while columns containing β, β'-oxydipropionitrile as the stationary phase were the most effective for the separation of saturated and unsaturated hydrocarbons of low boiling points. For the analysis of carbonyl compounds of low boiling points tricresyl phosphate, at higher temperatures the less selective apiezon and silicone greases were chosen. For a reliable analysis of the gaseous and liquid products, the same experiment had to be repeated with differently packed columns. Peaks were generally identified by the injection of known substances.

For quantitative evaluation of the chromatograms, the areas were measured and calibration curves were used. The relative transformation rate of the oxetanes was followed by measuring the quantity of unconverted oxetanes as the function of the temperature.

SUMMARY

The thermal degradation of 2-monosubstituted oxetanes has been studied by the microreactor technique. The rate of thermolysis is a function of the resultant of the inductive and hyperconjugative effects of the hydrocarbon groups in α-position. The formation of the pyrolysis products may be explained as a result of two primary and some secondary processes. The main direction of thermal decomposition (80—90%) is a reaction starting with the splitting of the C—O bond next to the substituent, which results in the formation of an alkene-1 and formaldehyde. The splitting of the oxetane molecule into two parts is accompanied by isomerization processes to give the corresponding aldehydes and α,β-unsaturated alcohols; these reactions are probably due to the wall effect of the microreactor.

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CHEMICAL TRANSFORMATIONS OF DIOLS AND CYCLIC ETHERS, XXVII

APPLICATION OF THE KISHNER—WOLFF REACTION TO THE SYNTHESIS OF α,α′-TETRAALKYL OR -ARYL SUBSTITUTED OXETANES AND TETRAHYDROFURANS

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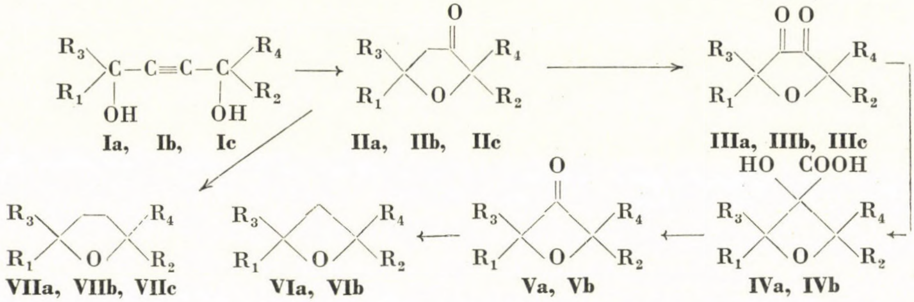
As part of our current researches, the chemical transformations of α,α′-tetrasubstituted four- and five-membered cyclic ethers (Types **VI** and **VII**) have been investigated. It is evident from the literature that the methods generally applied to the synthesis of cyclic ethers — ring closure of halohydrins in alkaline medium, and the electrophilic elimination reaction of diols — are not suitable for the preparation of the above compounds, especially of oxetanes, owing to the presence of a functional group in tertiary position.

In these reactions primarily diolefins, olefin alcohols and in the case of 1,3-difunctional systems also other fragments are produced [1]. Consequently, the preparation of α,α′-tetrasubstituted cyclic ethers — and within this group mainly the synthesis of oxetanes —must utilize such starting materials that already contain the desired ring. The unnecessary functional group is eliminated in the last phase of the synthesis to obtain the desired ether.

As the α,α′-tetrasubstituted derivatives of tetrahydrofuran-3-one (Type **II**) and oxetane-3-one (Type **V**) are relatively easily accessible, these compounds were chosen as initial materials for the preparation of the corresponding cyclic ethers. The initial materials **I**—**V**, **VIII**, **IX** were prepared according to literature data (see, Experimental). The Kishner—Wolff method seemed to be the most appropriate for the reduction of the carbonyl group to methylene group, as this method is both simple and selective.

The following compounds have been prepared: the 2,2,4,4-tetramethyl (**VI**a) and 2,2-dimethyl-4,4-diethyl (**VI**b) derivatives of oxetane, the 2,2,5,5-tetramethyl (**VII**a), a 2,2-dimethyl-5,5-diethyl (**VII**b) and 2,5-bis-pentamethylene (**VII**c) derivatives of tetrahydrofuran; the starting materials were the corresponding homologues of butyne-(2)-diol-(1,4):



where

Ia—VIIa: $R_1 = R_2 = R_3 = R_4 = CH_3$;

Ib—VIIb: $R_1 = R_2 = CH_3$; $R_3 = R_4 = C_5H_5$;

Ic, IIc, IIIc, VIIc: $R_1 + R_3 = R_2 + R_4 = (CH_2)_5$.

We intended also to synthesize 2,4-bis-pentamethylene-oxetane, but the attempted benzilic acid rearrangement of 2,2,5,5-bis-pentamethylenetetrahydrofurandione-3,4 (**IIIc**) failed.

For reduction of the carbonyl to methylene group, the KISHNER—WOLFF process was used as modified by HUANG—MINLON [2]. This reaction gave the above described cyclic ethers in 70—80% yield. The cyclic ethers were identified by gas chromatography and microanalysis.

2,2,4,4-Tetraphenyl-oxetane was prepared in considerably lower yield (about 40%) by the KISHNER—WOLFF reduction of 2,2,4,4-tetraphenyl-oxetanone-3. The lower yield is due to the considerably lower rate of formation of the hydrazone than in the case of tetraalkyl-oxetanones (98—100% hydrazine hydrate must be used), and thus, under the experimental conditions, the base-catalyzed (potassium hydroxide, sodium triethyleneglycolate) decomposition of oxetanone may also take place simultaneously [3]. The synthesis of 2,2,4,4-tetraphenyl-oxetanone (**IX**) proceeds from benzaldehyde *via* benzoin, benzil, ethyldiphenylacetate and tetraphenylacetone (**VIII**); the reaction of **VIII** under the conditions of the KISHNER—WOLFF reduction is shown below (**VIII** → **X**):

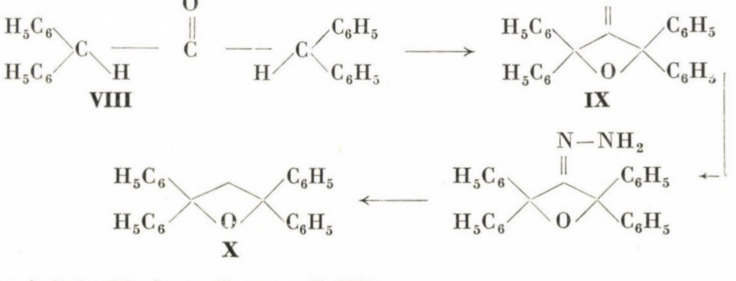
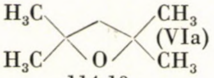
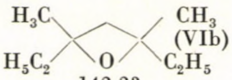
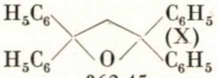
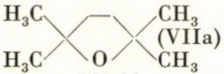
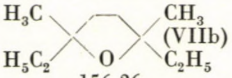


Table I

No.	Formula and molecular weight	Yield, %	B.p. °C (mmHg)	n_D^{20}	C %		H %	
					Found	Calc.	Found	Calc.
1.	 (VIa) 114.18	72	114 (758)	1.4022	73.48	73.63	12.10	12.38
2.	 (VIb) 142.23	78	152 (758)	1.4368	75.60	75.99	12.67	12.75
3.	 (X) 362.45	40	m.p. 59	—	88.69	89.50	6.33	6.07
4.	 (VIIa) 128.21	66	117 (754)	1.4036	74.78	74.94	12.44	12.58
5.	 (VIIb) 156.26	72	162 (756)	1.4401	76.94	76.91	12.85	12.82
6.	 (VIIc) 208.33	70	95 (2)	1.4856	80.23	80.77	11.20	11.54

Experiments have shown that the oxetanone → oxetane (**V** → **VI**, **IX** → **X**) and the tetrahydrofuranone → tetrahydrofuran (**II** → **VII**) reactions may be carried out in good yields, thus the Kishner—Wolff reduction may be applied to the preparation of cyclic ethers, and opens a way for the synthesis of new α,α'-tetrasubstituted oxetanes. Table I lists the yields of some cyclic ethers prepared by the Kishner—Wolff reaction, the results of the microanalyses, and the more important physical constants.

Experimental

2,5-*Dimethylhexyne*-3-*diol*-2,5 (**Ia**) was prepared by the method described in [3]. Starting with 0.05 mole of Mg, 24.5 g (70%) of diol was obtained. After recrystallization from carbon tetrachloride, the melting point of the product was 95° (lit. m.p. [4]: 95°).

2,2,5,5-*Tetramethyltetrahydrofuranone*-3 (**IIa**) [5, 6] was obtained in 85% yield (17 g) from 20 g of Ia, b.p. 149°; $n_D^{25} = 1.4182$ (lit. b.p. [6]: 149—149.5° at 762 mmHg; $n_D^{20} = 1.4202$). The melting point of 2,2,5,5-tetramethyltetrahydrofuran-3-one hydrazone was 125°.

(Found: C 61.72, H 9.98, N 11.69. Calc. for $C_8H_{16}ON_2$: C 61.70; H 10.28; N 11.9%).

2,2,5,5-*Tetramethyltetrahydrofuran-dione*-3,4 (**IIIa**) was prepared through 2,2,5,5-tetramethyl-4,4-dibromotetrahydrofuranone-3 [5] and also directly by oxidation with selenium dioxide [6]. This latter method was preferred because of its higher yield and greater simplicity. From 142 g (1 mole) of IIa, 276 g (92%) of the dibromo derivative was obtained, m.p. 52°. (Found: Br 52.8. Calc. for $C_8H_{12}O_2Br_2$: Br 53.3%). From 0.35 mole of the dibromo derivative (according to [7]) 16 g (56%) of **IIIa** was obtained. Oxidation with selenium dioxide (according to [6]) yielded, from 14.2 g (0.1 mole) of **IIa**, 11.2 g (73%) of **IIIa**. The melting point of the raspberry-coloured crystals was 56° (lit. m.p. [6]: 54—56°).

2,2,4,4-Tetramethyl-3-hydroxy-3-carboxy-oxetane (**IVa**) [7] was obtained in 77% yield (9.4 g) from 12 g (0.13 mole) of **IIIa** after recrystallization from chloroform. M.p. 118° (lit. m. p. [7]: 112°).

2,2,4,4-Tetramethyl-oxetanone-3 (**Va**) was prepared according to [7]. Sublimation in vacuum of 40 g (0.22 mole) of **IVa** gave 12 g (43%) of **Va**, m.p. 47.5° (lit. m.p. [7]: 48°).

2,2,4,4-Tetramethyl-oxetane (**VIa**) was prepared by heating a mixture of 2.6 g (0.02 mole) of 2,2,4,4-tetramethyl-oxetane-3-one, 30 ml of triethylene glycol, 4.5 ml (0.04 mole) of 62% hydrazine hydrate, and 4 g of potassium hydroxide at 100° for 1 hr. (the thermometer was immersed in the liquid). The temperature of the reaction mixture was then slowly raised (within about 2 hrs.) to 170°, during which time approximately 5 ml of a turbid liquid distilled over, the upper layer being the organic phase. The aqueous phase was extracted with ether, the ether extract combined with the organic phase and the mixture dried over sodium sulphate. Distillation gave 1.64 g (72%) of a colourless liquid (for its physical constants, see Table I). Gas-liquid chromatographic analysis was carried out under the following conditions: 1. 1 Apiezon grease; 2. 160; 3. He 50; 4. 200; 5. 1200.* The peak appeared at 4.9 cm from the point of injection.

2,2,5,5-Tetramethyltetrahydrofuran (**VIIa**) was prepared from **IIa** by the method described for **VIa**. From 4.26 g of IIa, 2.47 g (66%) of **VIa** was obtained (for the physical constants of the compound, see Table I). (Literature data [15]: b.p. 116—117° at 754 mmHg; $n_D^{20} = 1.4012$). Gas-liquid chromatographic analysis: 1. 3 Silicon grease; 2. 160; 3. He 50; 4. 140; 5. 1200. **VIIa** appeared at 9 cm from the point of injection.

3,6-Dimethyloctyne-4-*diol-3,6* (**Ib**) was prepared by the method described in [4]. Melting point: 54° (lit. m.p. [16]: 54°).

2,5-Dimethyl-2,5-diethyltetrahydrofuranone-3 (**IIb**) was prepared similarly to **IIa**. From 21 g of the diol, 14.5 g (70%) of **IIb** was obtained, b.p. 194° at 758 mm Hg (lit. b.p. [8]: 190—196°).

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* Here, as well as throughout the experiments described, the conditions of gas-liquid chromatography are given in the following order: 1. the stationary phase in a 1 m long column (15%) on thermolite; 2. temperature of the thermostat; 3. nature and rate of the carrier gas (in ml per min.); 4. the detector current (mA); 5. rate of the paper (mm per hour). A *Willy Giede Type GCHF* 18/2 apparatus was used.

2,5-Dimethyl-2,5-diethyltetrahydrofuran-3,4-dione (**IIIb**) was prepared by oxidation with selenium dioxide as described for **IIIa**. 31 g (0.25 mole) of **IIb** gave 26 g (66%) of **IIIb**, b.p. 64—66° at 2 mmHg (lit. b.p. [8]: 56—63° at 1 mm Hg).

2,4-Dimethyl-2,4-diethyl-3-hydroxy-3-carboxy-oxetane (**IVb**) was prepared similarly to **IVa**. From 40 g of **IIIb**, 19.2 g (45%) of **IVb** was obtained. Recrystallization from carbon tetrachloride gave m.p. 128°. (Lit. m.p. [8]: 127—128°.) (Found: C 59.58, H 8.87. Calc. for $C_{10}H_{18}O_4$: C 59.45, H 8.92%).

2,4-Dimethyl-2,4-diethyloxetanone-3 (**Vb**) was prepared in the same way as described for **Va**. 30 g (0.14 mole) of **IVb** gave 14.5 g (69%) of **Vb**, m.p. 56° (lit. m.p. [8]: 56—57°). (Found: C 69.68, H 9.96. Calc. for $C_9H_{16}O_2$: C 69.87, H 10.26%).

2,4-Dimethyl-2,4-diethyl-oxetane (**VIb**) (a mixture of the *cis* and *trans* isomers) was prepared as described for **VIa**. 3.2 g (0.02 mole) of the oxetanone gave 2.2 g (78%) of oxetane (for the physical constants of the compound, see Table I). The conditions of gas-liquid chromatography were the same as for compound **VIa**, the double peak appeared at 13 cm from the place of injection.

2,5-Dimethyl-2,5-diethyltetrahydrofuran (**VIIb**) (a mixture of the *cis* and *trans* isomers) was prepared from **IIb** in the way described for **VIa**. From 3.4 g (0.02 mole) of the initial substance, 2.3 g (72%) of **VIIb** was obtained. (For the physical constants of the compound, see Table I.) (Lit. b.p. [17]: 161—163°; n_D^{25} 1.4378).

1,1′-Ethynylenebicyclohexanol (**Ic**) was prepared by the method described in [9]. 255 g of cyclohexanone gave 156 g (52%) of diol. After recrystallization from carbon tetrachloride, the melting point of the compound was 111° (lit. m.p. [9]: 109—111°).

2,2,5,5-Bis-pentamethylenetetrahydrofuranone (**IIc**) was prepared according to [10]. 20 g of the diol gave 14.8 g (74%) of **IIc**, b.p. at 5 mm Hg 130—131°; $n_D^{20} = 1.4933$ (lit. b.p. [10]: 141—142° at 9 mmHg; $n_D^{20} = 1.4941$). Gas-liquid chromatographic analysis: 1. 1 Silicone grease; 2. 180; 3. 120 He; 4. 140; 5. 600. The peak appeared at 2.3 cm from the point of injection.

2,2,5,5-Bis-pentamethylenetetrahydrofuran (**VIIc**) was prepared by the method described for **VIa**. 3.3 g (0.015 mole) of **IIc** gave 2.2 g (70%) of **VIIc** by distillation up to 210°, and subsequent purification. (For the physical constants of the compound, see Table I: lit. b.p. [11]: 93—95° at 2 mm Hg.) Gas-liquid chromatographic analysis: 1. 2 Silicone grease (NaCl); 2. 160; 3. 90 He; 4. 180; 5. 600. The peak appeared at 5.5 cm from the point of injection.

Benzoin, Benzilic acid, diphenylacetic acid and ethyl diphenylacetate were prepared by the methods described in the literature [12, 13].

Tetraphenylacetone (**VIII**) was prepared according to [14]. 60 g of ethyl diphenylacetate gave 16.5 g (37%) of **VIII**; 16 g (30%) of diphenylacetic acid was recovered. M.p. of **VIII**: 134° (lit. m.p. [14]: 133—134°).

2,2,4,4-Tetraphenyl-oxetanone (**IX**) was prepared by the method described in [3]. Oxygen was allowed to pass through 50 ml of a 91% acetic acid solution of 5 g of tetraphenylacetone at 107—110°, and the crude product was worked up to obtain 3.2 g (62%) of oxetanone. Recrystallization from acetone gave m.p. 200.5° (lit. m.p. [3]; 199—201°).

2,2,4,4-Tetraphenyl-oxetane (**X**) was prepared as follows: A mixture of 30 ml of 62% hydrazine hydrate, 30 ml of ethylene glycol, and 30 ml of xylene was placed into a 100 ml flask with a side arm, and the xylene was distilled off entraining the water which diluted the hydrazine hydrate. The flask was cooled, and 3.8 g (0.01 mole) of 2,2,4,4-tetraphenyloxetane-3--one was added. The temperature of the reaction mixture was raised to 180—190°, then cooled, and 4 g of potassium hydroxide or sodium triethyleneglycolate (prepared from 1 g of Na and 20 ml of triethylene glycol) was added. The mixture was refluxed at 190—200° for 7—8 hrs., during which time about 4—5 ml of a turbid liquid distilled over. After cooling, 100 ml of cold water was added, and the mixture was allowed to stand for one day. The crystals were filtered off and recrystallized from 50% ethyl alcohol to obtain 1.38 g (38%) of the product, m.p. 58—59°. No attempt was made to isolate and analyze the by-products.

SUMMARY

The following cyclic ethers have been prepared from the corresponding oxetanone and tetrahydrofuranone homologues by KISHNER—WOLFF reduction: 2,2,4,4-tetramethyloxetane (72% yield); 2,4-dimethyl-2,4-diethyl-oxetane (78%); 2,2,4,4-tetraphenyloxetane (40%); 2,2,5,5-tetramethyltetrahydrofuran (66%); 2,5-dimethyl-2,5-diethyltetrahydrofuran (72%); and 2,2,5,5-bis-pentamethylenetetrahydrofuran (70%).

This represents a new method for the synthesis of α,α′-tetrasubstituted four-membered cyclic ethers otherwise accessible with difficulty. The syntheses also represent an extension of the scope of the KISHNER—WOLFF method of reduction.

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POLYMERISATION DES METHYLMETHACRYLATS BEI HOHEN UMSÄTZEN, II

UNTERSUCHUNG DER INITIALWIRKUNG VON LAUROYLPEROXYD

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Eingegangen am 6. Dezember 1965

Bei der Blockpolymerisation des Methylmethacrylats hängt die durch den Geleffekt verursachte Geschwindigkeitszunahme von der Initiatorkonzentration ab [1]. In der vorliegenden Arbeit wird die Untersuchung der Wirkung der Variierung des Initiators auf die Geschwindigkeit der bei hohen Umsätzen durchgeführten Polymerisation beschrieben.

Bei der Untersuchung der Anfangsgeschwindigkeit der Polymerisation konnte nachgewiesen werden, daß die Aktivierungsenergie des Zerfalls verschiedener Initiatoren und die Wirksamkeit der Initiierung unterschiedlich waren. Folglich fand man unter konstanten Bedingungen, aber bei verschiedenen Initiatorkonzentrationen gleiche Polymerisationsgeschwindigkeiten. Mit dem Fortschreiten der Polymerisation nimmt die Initiatorkonzentration ab, und auch die Wirksamkeit der Initiierung ändert sich [2, 3]. Das Maß der Änderung hängt ebenfalls von der Art des Initiators ab.

Rafikow und Gladyschew konnten zeigen [4], daß die verschiedenen Initiatoren die Geschwindigkeit der bei hohen Umsätzen durchgeführten Polymerisation unterschiedlich beeinflussen. In gewissen Fällen ändert die Verminderung der Initiatorkonzentration auch den Charakter der Zeit-Umsatz-Kurven, in Gegenwart anderer Initiatoren jedoch verändert die Verminderung der Initiatorkonzentration nur die Polymerisationsgeschwindigkeit, und der Charakter der Kurven bleibt konstant.

In unserer Arbeit untersuchten wir die Blockpolymerisation des Methylmethacrylats in Gegenwart von Lauroylperoxyd. Obwohl man Lauroylperoxyd in der Industrie als Initiator weitverbreitet verwendet, ist seine Initialwirkung auf die Blockpolymerisation des Methylmethacrylats noch nicht untersucht worden.

Experimenteller Teil

Bezüglich der Versuchsmethodik und der Reinigung des Monomers verweisen wir auf unsere vorangegangene Mitteilung [1]. Auch das Lauroylperoxyd reinigten wir auf die gleiche Weise wie das Benzoylperoxyd. Der Schmelzpunkt des umkristallisierten Initiators (nach der Mikromethode von Kofler bestimmt) betrug 55 °C.

Ergebnisse

Unsere Versuche führten wir bei 50, 60 und 70 °C durch, als Beispiel sind auf Abb. 1 die in den bei 50 °C durchgeführten Versuchen erhaltenen Zeit-Umsatz-Kurven gezeigt. Zur Bestimmung der Anfangsgeschwindigkeit

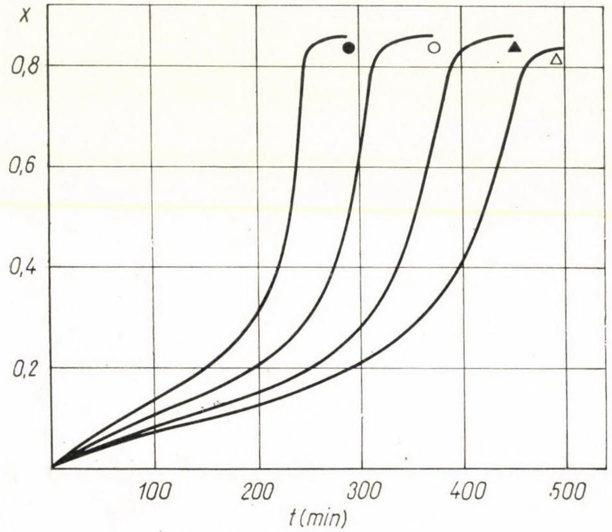

Abb. 1. Zeit-Umsatz-Kurven für die Polymerisation bei 50 °C. Initiatorkonzentration: (●): 2,72 · 10^{-2} mol l^{-1}; (○): 1,39 · 10^{-2} mol l^{-1}; (▲): 7,76 · 10^{-3} mol l^{-1}; (△): 5,03 · 10^{-3} mol l^{-1}

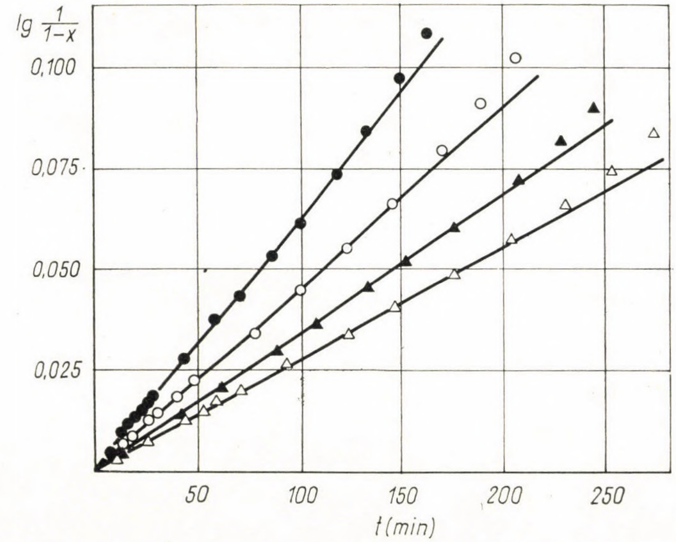

Abb. 2. Einfluß der Änderung der Initiatorkonzentration auf die Anfangsgeschwindigkeit der Polymerisation bei 50 °C

Tabelle I

Charakteristische Daten der mit Lauroylperoxyd initiierten Polymerisation

Temperatur	i mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50 °C	$2.72 \cdot 10^{-2}$	$2{,}24 \cdot 10^{-4}$	0,39	0,394	0,860
50 °C	$1{,}39 \cdot 10^{-2}$	$1{,}61 \cdot 10^{-4}$	0,26	0,370	0,865
50 °C	$7{,}76 \cdot 10^{-3}$	$1{,}22 \cdot 10^{-4}$	0.18	0,370	0,860
50 °C	$5{,}03 \cdot 10^{-3}$	$9{,}92 \cdot 10^{-5}$	0,14	0,368	0,860
60 °C	$9{,}04 \cdot 10^{-3}$	$3{,}09 \cdot 10^{-4}$	0,44	0,387	0,870
60 °C	$5{,}06 \cdot 10^{-3}$	$2{,}28 \cdot 10^{-4}$	0,13	0,377	0,880
60 °C	$3{,}35 \cdot 10^{-3}$	$1{,}88 \cdot 10^{-4}$	0,23	0,373	0,885
60 °C	$2{,}26 \cdot 10^{-3}$	$1{,}56 \cdot 10^{-4}$	0,18	0,368	0,890
70 °C	$2{,}24 \cdot 10^{-3}$	$3{,}59 \cdot 10^{-4}$	0,27	0,350	0,910
70 °C	$1{,}39 \cdot 10^{-3}$	$2{,}85 \cdot 10^{-4}$	0,20	0,348	0,895
70 °C	$9{,}86 \cdot 10^{-4}$	$2{,}44 \cdot 10^{-4}$	0,16	0,345	0,880
70 °C	$6{,}84 \cdot 10^{-4}$	$2{,}00 \cdot 10^{-4}$	0,13	0,340	0,890

der Polymerisation sind die Werte von $\lg \frac{1}{1-x}$ als Funktion der Zeit dargestellt. Die erhaltenen Geraden, aus deren Anstieg die Anfangsgeschwindigkeit der Polymerisation berechnet wurde, zeigt Abb. 2, die zu allen Temperaturen und Initiatorkonzentrationen gehörenden Zahlenwerte sind in Tabelle I aufgeführt. Aus den Anfangsgeschwindigkeiten bestimmten wir die Brutto-Geschwindigkeitskonstanten der Polymerisation, für die sich bei 50 °C $1{,}46 \cdot 10^{-4}\ \mathrm{mol}^{-\frac{1}{2}}\mathrm{l}^{\frac{1}{2}}\mathrm{sec}^{-1}$, bei 60 °C $3{,}44 \cdot 10^{-4}\ \mathrm{mol}^{-\frac{1}{2}}\mathrm{l}^{\frac{1}{2}}\mathrm{sec}^{-1}$ und bei 70 °C $8{,}10 \cdot 10^{-4}\ \mathrm{mol}^{-\frac{1}{2}}\mathrm{l}^{\frac{1}{2}}\mathrm{sec}^{-1}$ ergab. Die aus den Brutto-Geschwindigkeitskonstanten berechnete Aktivierungsenergie (E) beträgt 18,8 kcal/mol.

Den Abschnitt der Polymerisation nach Auftreten des Geleffekts werteten wir auf Grund der Gleichung von SAWADA [5] aus. Nach der Gleichung erhält man bei der Darstellung der Werte von $\frac{1}{x_2 - x_1} \ln \frac{x - x_1}{x_2 - x}$ als Funktion der Zeit Geraden, die die Abb. 3 zeigt. In unserer vorangegangenen Mitteilung [1] verwendeten wir die Gleichung von SAWADA in einer anderen Form, für die die mathematische Auswertung zwar einfacher ist, die aber den für die durch den Geleffekt verursachte Geschwindigkeitszunahme charakteristischen K_1-Wert als Produkt ergibt. Der Umstand, daß im Produkt $K_1(x_2 - x_1)$ die physikalische Bedeutung der einzelnen Glieder unterschiedlich ist, wirkt störend. Daher ist es richtiger, mit der im vorliegenden Fall verwendeten Auswertungsmethode zu arbeiten.

In Gegenwart von Lauroylperoxyd erhielten wir ähnliche Grenzumsatz-Werte (x_2) wie mit Benzoylperoxyd. Die Abhängigkeit des Grenzumsatzes von der Initiatorkonzentration und der Temperatur ist gleichfalls ähnlichen Charakters. Der für den Beginn des Geleffekts charakteristische Umsatzgrad ist in jedem Fall größer, und ändert sich in wesentlich geringerem Maße mit den erwähnten Parametern, als dies in Gegenwart von Benzoylperoxyd beobachtet werden konnte.

Die Änderung der Anfangsgeschwindigkeit der Polymerisation und des K_1-Wertes als Funktion der Initiatorkonzentration wird auf Abb. 4 gezeigt. Auf Grund der Versuchsergebnisse ist die Anfangsgeschwindigkeit der Polymerisation der Quadratwurzel der Initiatorkonzentration proportional. Die für die Polymerisation bei hohen Umsätzen charakteristischen K_1-Werte sind der 0,62-sten Potenz der Initiatorkonzentration proportional, d. h. der Wert des Exponenten verschiebt sich gegen 1, wie dies wegen der Behinderung der bimolekularen Abbruchsreaktion auch zu erwarten war.

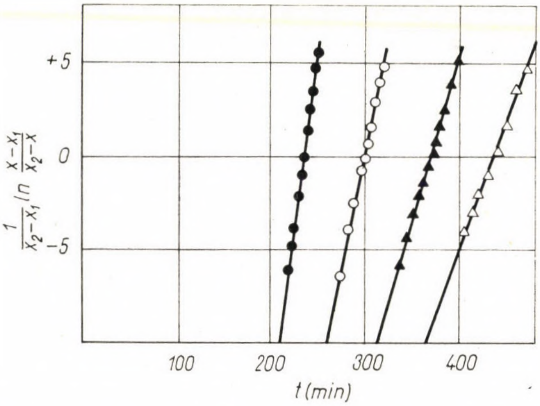

Abb. 3. Einfluß der Änderung der Initiatorkonzentration auf die Polymerisation bei hohen Umsätzen. Temperatur: 50 °C

Es wurde nun untersucht, in welchem Maße die für die Geleffekt-bedingte Geschwindigkeitszunahme charakteristischen K_1-Werte bei gleicher Anfangsgeschwindigkeit ($W_{st} = 2 \cdot 10^{-4}$ mol l^{-1} sec^{-1}) durch die Qualität des Initiators und durch die Temperatur beeinflußt werden. Die in Tabelle II für Lauroylperoxyd angegebenen Daten berechneten wir auf Grund der Abb. 4, die Daten für Benzoylperoxyd aus unserer vorangegangenen Mitteilung [1]. Wie man aus Tabelle II sieht, besteht hinsichtlich der K_1-Werte kein wesentlicher Unterschied zwischen den beiden Initiatoren. Demgegenüber ist im Anfangsabschnitt der Polymerisation — wie dies aus einem Vergleich der Brutto-Geschwindigkeitskonstanten hervorgeht — die Polymerisationsgeschwindigkeit in Gegenwart von Lauroylperoxyd etwa um 60—70% größer.

Tabelle II

Die Werte von K_1 bei den zur Anfangsgeschwindigkeit von $2 \cdot 10^{-4}$ mol l^{-1} sec^{-1} gehörenden Initiatorkonzentrationen

Temperatur:		50 °C	60 °C	70 °C
Benzoylperoxyd	i (mol l^{-1}):	$5{,}90 \cdot 10^{-2}$	$9{,}50 \cdot 10^{-3}$	$1{,}73 \cdot 10^{-3}$
	K_1:	0,33	0,19	0,10
Lauroylperoxyd	i (mol l^{-1}):	$2{,}12 \cdot 10^{-2}$	$3{,}80 \cdot 10^{-3}$	$6{,}84 \cdot 10^{-4}$
	K_1:	0,34	0,25	0,13

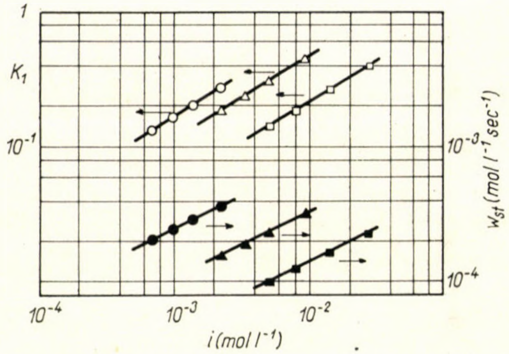

Abb. 4. Abhängigkeit der Anfangsgeschwindigkeit der Polymerisation und der K_1-Werte von der Initiatorkonzentration. Temperatur: (□): 50 °C, (△): 60 °C, (○): 70 °C

Es kann also festgestellt werden, daß in diesem Fall die Qualität des Initiators die Polymerisationsgeschwindigkeit im Anfangsabschnitt der Polymerisation weit mehr beeinflußt, als im Bereich hoher Umsätze. Dagegen spielt im Abschnitt der Polymerisation nach Auftreten des Geleffekts die Änderung der Temperatur eine größere Rolle.

ZUSAMMENFASSUNG

Die mit Lauroylperoxyd initiierte Blockpolymerisation von Methylmethacrylat wurde bei verschiedenen Temperaturen untersucht und die Brutto-Geschwindigkeitskonstanten sowie die Aktivierungsenergie der Reaktion bestimmt. Es zeigte sich, daß der Grenzumsatz mit der Initiatorkonzentration und der Temperatur in ähnlichem Zusammenhang steht wie in Gegenwart von Benzoylperoxyd, während sich der Beginn des Geleffekts mit dem vorgenannten Parameter in wesentlich geringerem Maße ändert. Ein Vergleich der beiden Initiatoren zeigte, daß die Änderung der Initiatorqualität die Polymerisationsgeschwindigkeit im Anfangsabschnitt der Polymerisation weit mehr beeinflußt als bei hohen Umsätzen.

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POLYMERISATION DES METHYLMETHACRYLATS BEI HOHEN UMSÄTZEN, III.

UNTERSUCHUNG DER VERZÖGERUNGSWIRKUNG VON MONONITROPHENOLEN

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Bei der Blockpolymerisation im technischen Maßstab läßt sich die Reaktion um so leichter handhaben, je besser es gelingt, die durch den Geleffekt verursachte Geschwindigkeitszunahme einzudämmen. Zur Feststellung der Möglichkeiten zur Verminderung des Geleffekts wurde der Ablauf der Polymerisation in Gegenwart von Verzögerern untersucht.

Die kinetische Untersuchung des Anfangsabschnittes der verzögerten Polymerisation knüpft sich in erster Linie an die Arbeiten von KICE [1], TÜDŐS [2, 3, 4] und BAGDASARJAN [5]. Alle drei Autoren haben festgestellt, daß die relative Polymerisationsgeschwindigkeit (der Quotient der in Gegenwart bzw. in Abwesenheit des Verzögerers gemessenen Polymerisationsgeschwindigkeiten) von der Konzentration des Verzögerers abhängig ist. Die Zusammenhänge weichen nur wegen der in den Ableitungen verwendeten unterschiedlichen vereinfachenden Annahmen voneinander ab.

Die Verzögerer vermindern nicht nur die Anfangsgeschwindigkeit der Polymerisation, sondern verändern auch den Ablauf der für den Reaktionsverlauf charakteristischen Zeit-Umsatz-Kurven und vermindern die Polymerisationsgeschwindigkeit auch bei hohen Umsätzen wesentlich. Die Untersuchung der verzögerten Polymerisation bei hohen Umsätzen ist ein noch unerschlossenes Gebiet, obwohl sie auch große praktische Bedeutung besitzt.

Experimenteller Teil

Die Versuchsmethoden sowie die Reinigung des Monomers und Initiators waren die gleichen wie in unserer vorangehenden Mitteilung [6] beschrieben. Die eingesetzten Mononitrophenole waren die folgenden:

2-Nitrophenol. Handelsübliches, analytisch reines Produkt, F. 45 °C.

3-Nitrophenol. Handelsübliches, analytisch reines Produkt, F. 96 °C.

4-Nitrophenol. Das handelsübliche, analytisch reine Produkt wurde aus Chloroform (Kp. 61,4—61,6 °C; n_D^{20}: 1,4459) umkristallisiert; F. 113 °C. Die Schmelzpunkte bestimmten wir nach der Mikromethode von KOFLER.

Ergebnisse

Unsere Versuche führten wir bei gleicher Initiatorkonzentration ($4{,}13 \cdot 10^{-2}$ mol/l), in Gegenwart von Verzögerern verschiedener Menge, bei 50 und 60 °C durch. Aus der Reihe der Zeit-Umsatz Beziehungen werden die in Gegenwart von 3-Nitrophenol erhaltenen Kurven in Abb. 1 gezeigt. Die in Gegenwart von 2-Nitrophenol und 4-Nitrophenol erhaltenen Kurven verlaufen ähnlich. Um die Anfangsgeschwindigkeit der Polymerisation bestimmen zu können,

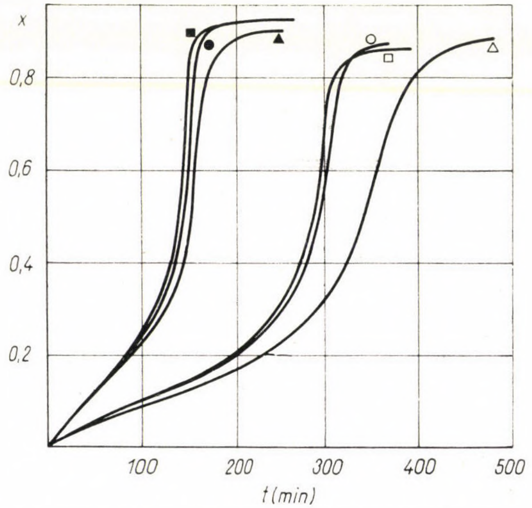

Abb. 1. Zeit-Umsatz-Kurven in Gegenwart von $4{,}13 \cdot 10^{-2}$ mol l^{-1} Benzoylperoxyd und verschiedenen Mengen 3-Nitrophenol. Verzögererkonzentrationen:

Temperatur 50 °C	Temperatur 60 °C
(□): $8{,}50 \cdot 10^{-3}$ mol l^{-1}	(■): $1{,}70 \cdot 10^{-2}$ mol l^{-1}
(○): $1{,}70 \cdot 10^{-2}$ mol l^{-1}	(●): $3{,}40 \cdot 10^{-2}$ mol l^{-1}
(△): $4{,}00 \cdot 10^{-2}$ mol l^{-1}	(▲): $6{,}80 \cdot 10^{-2}$ mol l^{-1}

sind die Werte von $\lg \frac{1}{1-x}$ als Funktion der Zeit dargestellt. Die erhaltenen Geraden, aus deren Anstieg wir die Anfangsgeschwindigkeit der Polymerisation berechneten, sind auf Abb. 2 ersichtlich. Die Tabellen, I, II und III enthalten die numerischen Werte der Anfangsgeschwindigkeit der Polymerisation.

Aus der Anfangsgeschwindigkeit berechneten wir den durch BAGDASARJAN [5] beschriebenen Verzögerungsparameter:

$$F = \frac{1 - Y^2}{Y}, \tag{1}$$

wobei der Verzögerungsparameter, F, eine dimensionslose Größe darstellt.

Der Wert von F wird um so größer, je stärker die verzögernde Wirkung in der Polymerisationsreaktion ist. In der Gleichung (1) ist

$$Y = \frac{W m_0}{W_0 m}. \qquad (2)$$

Hier bedeuten W die Polymerisationsgeschwindigkeit in Gegenwart des Verzögerers, W_0 die in Abwesenheit von Verzögerern gemessene Polymerisationsgeschwindigkeit und m sowie m_0 die Monomerkonzentrationen unter ebensolchen Bedingungen. Mit der Abnahme der Verzögerer-Konzentration nähert

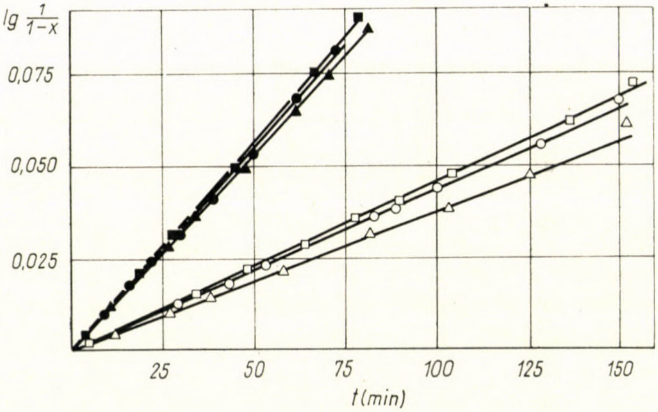

Abb. 2. Einfluß der Änderung der Konzentration von 3-Nitrophenol auf die Anfangsgeschwindigkeit der Polymerisation

Tabelle I

Charakteristische Daten der Polymerisation in Gegenwart von 2-Nitrophenol
Benzoylperoxydkonzentration: 4,13 · 10^{-2} mol/l

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50 °C	1,06 · 10^{-3}	1,670 · 10^{-4}	0,208	0,33	0,87
50 °C	2,83 · 10^{-3}	1,646 · 10^{-4}	0,056	0,24	0,88
50 °C	4,25 · 10^{-3}	1,622 · 10^{-4}	*	*	*
60 °C	1,06 · 10^{-3}	3,875 · 10^{-4}	0,375	0,37	0,93
60 °C	2,83 · 10^{-3}	3,623 · 10^{-4}	0,189	0,34	0,92
60 °C	4,25 · 10^{-3}	3,465 · 10^{-4}	0,131	0,30	0,91

* bei hohen Umsätzen sank die Polymerisationsgeschwindigkeit derart, daß keine Daten mehr bestimmt werden konnten.

Tabelle II

Charakteristische Daten der Polymerisation in Gegenwart von 3-Nitrophenol
Benzoylperoxydkonzentration: 4,13 · 10^{-2} mol/l

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50 °C	8,50 · 10^{-3}	1,607 · 10^{-4}	0,175	0,32	0,87
50 °C	1,70 · 10^{-2}	1,528 · 10^{-4}	0,154	0,31	0,88
50 °C	4,00 · 10^{-2}	1,386 · 10^{-4}	0,075	0,27	0,89
60 °C	1,70 · 10^{-2}	3,938 · 10^{-4}	0,465	0,37	0,93
60 °C	3,40 · 10^{-2}	3,859 · 10^{-4}	0,355	0,37	0,93
60 °C	6,80 · 10^{-2}	3,701 · 10^{-4}	0,206	0,30	0,90

sich der Wert von m_0/m eins. Bei entsprechend niedrigen Verzögererkonzentrationen braucht man daher die Änderung der Monomerkonzentration nicht zu berücksichtigen. Es wurde experimentell nachgewiesen [5], daß F im Bereich niedriger Verzögererkonzentrationen z/W_0 proportional ist, wenn z die Verzögererkonzentration bedeutet.

Auf dieser Grundlage sind die aus unseren in Gegenwart von 3-Nitrophenol durchgeführten Messungen berechneten Verzögerungsparameter auf Abb. 3 als Funktionen von z/W_0 angegeben. Ähnliche Geraden erhielten wir auch mit den beiden anderen Mononitrophenolen. Den Anstieg der erhaltenen Geraden, die für die Wirksamkeit der untersuchten Verzögerer charakteristisch sind, enthält die Tabelle IV. Die Werte der zur Berechnung der Verzögerungsparameter notwendigen, zur Benzoylperoxydkonzentration von 4,13 · 10^{-2} mol/l gehörenden Anfangsgeschwindigkeiten: $W_0 = 1{,}685 \cdot 10^{-4}$ mol/l/sec bei 50 °C sowie $W_0 = 4{,}016 \cdot 10^{-4}$ mol/l/sec bei 60 °C sind aus der Mitteilung [6] übernommen.

Tabelle III

Charakteristische Daten der Polymerisation in Gegenwart von 4-Nitrophenol
Benzoylperoxydkonzentration: 4,13 · 10^{-2} mol/l

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50 °C	8,50 · 10^{-3}	1,638 · 10^{-4}	0,149	0,33	0,88
50 °C	1,70 · 10^{-2}	1,607 · 10^{-4}	0,107	0,30	0,88
50 °C	3,40 · 10^{-2}	1,528 · 10^{-4}	0,073	0,30	0,92
60 °C	8,50 · 10^{-3}	3,969 · 10^{-4}	0,418	0,37	0,92
60 °C	1,70 · 10^{-2}	3,922 · 10^{-4}	0,374	0,37	0,92
60 °C	3,40 · 10^{-2}	3,796 · 10^{-4}	0,250	0,33	0,93

Der Abschnitt der Polymerisation nach Auftreten des Geleffekts wurde auf Grund der Gleichung von SAWADA [7] ausgewertet. Bei der Darstellung der Werte von $\frac{1}{x_2 - x_1} \ln \frac{x - x_1}{x_2 - x}$ als Funktion der Zeit erhalten wir Geraden, die auf Abb. 4 gezeigt sind. Die Anstiege der Geraden ergeben die für die durch den Geleffekt verursachte Geschwindigkeitszunahme charakteristischen K_1-Werte, die gemeinsam mit den x_1- und x_2-Werten in den Tabellen I, II und III zusammengefaßt sind. Wie aus den Tabellen hervorgeht, wird mit Zunahme der Verzögererkonzentration der Umsatzgrad x_1, bei dem der Geleffekt auf-

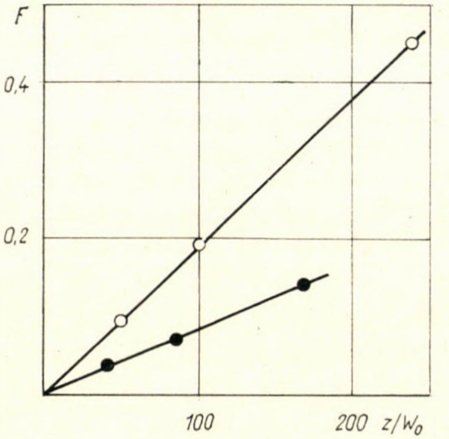

Abb. 3. Abhängigkeit der Verzögerungsparameter von den z/W_0-Werten in Gegenwart von 3-Nitrophenol. (○): Temperatur 50 °C (●): Temperatur 60 °C

Tabelle IV

Verzögerungswirkung von Mononitrophenolen im Anfangsabschnitt der Polymerisation

	Temperatur	$\frac{F W_0}{z} \, 10^2$
2-Nitrophenol	50 °C	0,30
	60 °C	2,85
3-Nitrophenol	50 °C	0,19
	60 °C	0,08
4-Nitrophenol	50 °C	0,10
	60 °C	0,12

tritt, kleiner. Der Grenzumsatz (x_2) ist keine eindeutige Funktion der Verzögererkonzentration, sie ist jedoch in einem gegebenen Konzentrationsbereich immer größer als bei gleicher Initiatorkonzentration und ohne Verzögerer. Bei niedrigerer Temperatur — unter sonst gleichen Bedingungen — wird auch der Grenzumsatz kleiner.

Bei hohen Umsätzen verwendeten wir zur Charakterisierung der Wirksamkeit der untersuchten Verzögerer die $K_{1,rel}$-Werte.

$$K_{1,rel} = \frac{K_1}{K_{1,0}}. \tag{3}$$

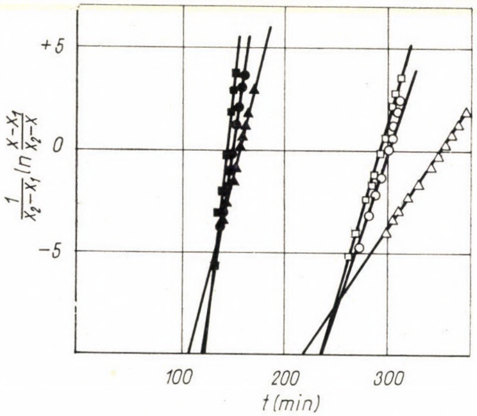

Abb. 4. Einfluß der Änderung der Konzentration von 3-Nitrophenol auf die Polymerisation bei hohen Umsätzen

K_1 ist hier der für die durch den Geleffekt verursachte Geschwindigkeitszunahme charakteristische Wert in Gegenwart eines Verzögerers bestimmter Qualität und Quantität, $K_{1,0}$ bedeutet das gleiche ohne Verzögerer. Die zur Berechnung von $K_{1,rel}$ notwendigen, zu einer Benzoylperoxydkonzentration von $4{,}13 \cdot 10^{-2}$ mol l^{-1} gehörenden Werte $K_{1,0} = 0{,}26$ bei 50 °C, und $K_{1,0} = 0{,}50$ bei 60 °C berechneten wir aus den Angaben der Mitteilung [6]. Die verschiedenen $K_{1,rel}$-Werte sind als Funktionen der Verzögererkonzentration in Abb. 5 gezeigt. Man sieht, daß mit zunehmender Verzögererkonzentration die $K_{1,rel}$-Werte stark abnehmen. Ein Vergleich der Polymerisationsgeschwindigkeiten mit den $K_{1,rel}$-Werten ergibt, daß die untersuchten Verzögerer die Polymerisationsgeschwindigkeit im Anfangsabschnitt der Polymerisation in weitaus geringerem Maße vermindern als bei hohen Umsätzen.

Als der wirksamste Verzögerer erwies sich das 2-Nitrophenol, seine Verzögerungswirkung ist sowohl im Anfangsabschnitt der Polymerisation als auch bei hohen Umsätzen allgemein um eine Größenordnung größer, als die der beiden anderen Verbindungen. Das ist damit zu erklären, daß die Wasserstoffbrücke zwischen den nebeneinander liegenden Nitro- und phenolischen Hydroxylgruppen eine gelockerte Elektronenstruktur verursacht, deren radikalische Reaktionsfähigkeit bedeutend größer ist. Zwischen der Wirksamkeit von 3-Nitrophenol und 4-Nitrophenol bestehen keine wesentlichen Unterschiede.

Die Änderung der Temperatur beeinflußt die Verzögerungswirkung der untersuchten Verbindungen. Dies zeigte sich im Anfangsabschnitt der Polymerisation am besten beim 2-Nitrophenol; bei den anderen beiden Verbindungen ist der Einfluß nicht bedeutend. Bei hohen Umsätzen ist zum Erreichen gleicher $K_{1,rel}$-Werte bei niedrigeren Temperaturen eine geringere Menge an Verzögerern notwendig. In diesem Fall fällt jedoch die Wirkung der Temperaturänderung in Gegenwart von 2-Nitrophenol weniger ins Auge als bei den anderen beiden Isomeren.

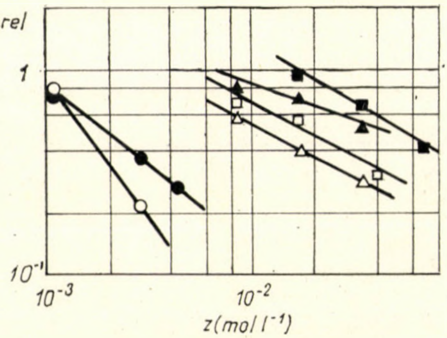

Abb. 5. Einfluß der Konzentrationsänderung des Verzögerers auf die $K_{1,rel}$-Werte
(○): 2-Nitrophenol bei 50 °C, (●): bei 60 °C
(□): 3-Nitrophenol bei 50 °C, (■): bei 60 °C
(△): 4-Nitrophenol bei 50 °C, (▲): bei 60 °C

ZUSAMMENFASSUNG

Die Blockpolymerisation des Methylmethacrylats wurde bei gleicher Initiatorkonzentration, in Gegenwart verschiedener Verzögerermengen untersucht. Die für die untersuchten Verbindungen charakteristischen Verzögerungsparameter wurden bestimmt. Die untersuchten Verbindungen vermindern die Polymerisationsgeschwindigkeit im Anfangsabschnitt der Polymerisation weit weniger als bei hohen Umsätzen. Der wirksamste Verzögerer war das 2-Nitrophenol, seine Verzögerungswirkung liegt um eine Größenordnung höher als die Wirkung der anderen beiden Verbindungen. Zwischen der Wirksamkeit von 3-Nitrophenol und 4-Nitrophenol sind keine wesenltichen Unterschiede festzustellen.

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COUNTERCURRENT DISTRIBUTION OF TRICHOMYCIN, CANDICIDIN AND HAMYCIN, THE HEPTAENE MACROLIDE ANTIFUNGAL ANTIBIOTICS OF AROMATIC SUBGROUP

(SHORT COMMUNICATION)

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In the course of an investigation of heptaene macrolide antifungal antibiotics Borowski [1], Khokhlova [2] and their co-workers compared the substances by paper chromatography (butanol : pyridine : water 6 : 4 : 5) and found them to fall into three categories. *(Candida albicans* was used for bioautographs.) Perimycin [1] proved to be the most mobile, candidin and amphothericin B [3] the least mobile, while trichomycin [4], candicidin [5] and levorin [6] occupied intermediate positions, differing very little from one another by this method. It was concluded [2] that candicidin and trichomycin were very similar and probably identical. Our paper chromatographic experiments (methanol : NH_3 : water 20 : 1 : 4) confirmed these findings.

On the other hand, Borowski [6] found that countercurrent distribution of the "aromatic" heptaenes trichomycin-A, candicidin and ascosin gave practically identical K values in a chloroform : methanol : borate buffer solvent system (pH 8.3).

Recently Divekar [7] has reported that hamycin [8], a heptaene macrolide antibiotic purified by countercurrent distribution, is very similar to trichomycin. Samples of poorer purity were reported to contain peptide moieties. The product purified by countercurrent distribution was free from amino acids. This observation has been fully confirmed by us.

The idea to compare trichomycin, candicidin and hamycin came to us on the basis of the above findings. These substances all belong to the aromatic subgroup of heptaene macrolide antifungal antibiotics, yielding on alkaline degradation p-aminoacetophenone, on acid hydrolysis mycosamine. Their absorption maxima are found at 340, 360, 382 and 402 nm. On basis of the spectral properties and paper chromatographic behaviour, we could not detect any difference in them, but their exact identity is not yet proved. Japanese investigators [9] attempted to separate trichomycin into fractions by alumina chromatography, but a sharp separation could not be achieved and besides a decomposition was caused by prolonged handling. Thus it seemed us reasonable to choose the countercurrent distribution method known to yield the best separation in this group of substances.

Our experiments were carried out in a 200-tube automatic apparatus. The aqueous layers (3 ml) were fixed by cellulose sponges regenerated from xanthogenate. The organic layers were chosen to be 6 ml [10], the distribution time was 4.5 minutes per tube. The solvent system consisted of chloroform : methanol : borate buffer 2 : 2 : 1 (pH 8.40) [9]. 100-mg samples of the starting material were employed.

The following substances were investigated:

trichomycin *(Grünenthal,* lot No. 114.),

candicidin *(International Center of Information on Antibiotics,* Liège, Belgium),

antibiotic S—515, isolated in our Institute (candicidin) having the same biological activity as trichomycin,

hamycin *(Hindustan Antibiotics Ltd.,* Pimpri, Poona, India),

amphothericin-B *(Fungizone, intravenous,* Squibb).

The maximum concentration tube number for trichomycin was 110. If the partition coefficient (K) is conventionally defined as the quotient of the concentrations in the lighter and heavier phases, this maximum concentration tube number corresponds to a K value of 1.64. In our apparatus invariably the more apolar phase is moving, independently of the specific weights. A smaller fraction gave a maximum activity in tube 145 ($K = 0.76$). The activities against *Candida albicans* and the extinction at 380 nm were determined to follow the distribution of the samples. Both methods gave the same maximum tube numbers. Two further maxima were found in tubes Nos. 50 and 65, without biological activity.

The maximum concentration tube number for candicidin was also 110, the activity being determined against *C. albicans* ($K = 1.64$). Spectrophotometric measurements at 380 nm gave maximum concentration in tube No. 115. No other biologically active fraction was detected.

Antibiotic S—515, prepared by us from the fermentation liquor of a *Streptomyces levoris* strain isolated in our Institute, was also submitted to countercurrent distribution. The maximum concentration tube number for this antibiotic was 110 ($K = 1.64$). No other biologically active fraction was found. The light absorption method gave the same maximum tube number, and two further maxima were detected in tubes Nos. 10 and 40. Thus antibiotic S—515 and candicidin are probably identical.

For hamycin, by determining the activity against *C. albicans* and the extinction at 380 nm, the maximum concentration tube number was also 110 ($K = 1.64$). A further, biologically inactive, small maximum was found in tube No. 30.

We compared the partition characteristics of aromatic heptaenes with amphothericin B [3], a member of the non-aromatic group, in order to check upon our method. The maximum concentration tube number for this antibiotic was 75 ($K = 3.33$), the activity being determined against *C. albicans*. Spectrophotometric measurements at 380 nm showed maximum concentration in tube No. 74. On the basis of the above results, the partition characteristics of aromatic and non-aromatic heptaenes show considerable differences, as it is also reflected by the literature [1].

The above distribution data lead to the conclusion that for the heptaene macrolides of aromatic subgroup (trichomycin, candicidin = S—515, and hamycin) the maximum concentration tube number is 110 according to biological determination. The values of the partition coefficients depend strongly upon the pH of the aqueous phase.

The maximum fractions of the substances mentioned were carefully converted into solids, taking care to avoid decomposition, and the solids were again submitted to countercurrent distribution. The 200-tube automatic apparatus was used; 50 mg of each antibiotic (trichomycin-A, candicidin = S—515, hamycin) was distributed simultaneously in one run in the system, applying the recycling technique in 200 tranfers. Trichomycin was loaded in tube No. 1, hamycin in tube No. 65 and finally candicidin (S—515) in tube No. 135. The distribution of the antibiotics was estimated both against *C. albicans* and spectrophotometrically. According to the former method the maximum concentration tube numbers for trichomycin, hamycin and candicidin were 109, 110, and 110; according to the latter method, 100, 116, and 116, respectively. Thus the activity curves and absorption curves differ to a certain extent.

On the basis of our results obtained by the countercurrent distribution method, the same substance is responsible for the biological (antifungal) activity in the main fraction of trichomycin, in candicidin (S—515) and in hamycin. There are, however, some differences in the biologically inactive contaminations.

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BOOK REVIEWS — BUCHBESPRECHUNGEN — РЕЦЕНЗИИ КНИГ

R. Belcher and C. L. Wilson: *New Methods of Analytical Chemistry*. Chapman and Hall, London, 1964, Second Edition pp. 366.

The book which surveys new developments in the most important branches of "classical,, analytical chemistry is the second, nearly entirely revised edition of the book of the authors published in 1955, and contains a great deal of new material.

The first chapter deals with standardizing substances, giving a detailed description of the properties, purification and use of chemicals recommended recently to standardize solutions employed for acid-base and redox titrations. This part is of interest to the analyst because many problems concerning standardizing substances have not been resolved so far.

Chapter 2, entitled "Indicators" deals with less known indicators, first of all with those possessing more advantageous properties than those used earlier, or those that can be used in relatively new branches of volumetric analysis, such as chemilunescent, special redox and metallofluorescent indicators. Chapter 3 treats the preparation and applications of some less common oxidizing and reducing standard solutions, such as ascorbic acid, hydrazine, lead tetraacetate, sodium chlorite, sodium vanadate, *etc.* Chapter 4 entitled "Organic Reagents" deals with new organic reagents used in gravimetric analysis, with complexing standard solutions analogous to sodium ethylenediamine tetraacetate and their applications, presenting some examples. This excellent survey is an entirely new part of the second edition. Chapter 6 treating selective spectrophotometric methods is also a new part of the book. Here are discussed some selected methods specific for a particular ion, or characterized by high sensitivity, or representing the solution of an old analytical problem. Chapter 7 dealing with precipitations from homogeneous solutions may well claim the interest of the analyst in view of the increasing importance of the method. Extraction methods have been gaining increasing importance in inorganic analysis; such methods are partly based on ionic association systems, and partly on the formation of chelate complexes. The main advantage of Chapter 8 dealing with these techniques is that it presents a clear picture of the most important possibilities for the determination of some ions by means of good tables. The last chapter of the book, Chapter 9, describes volumetric and gravimetric methods for the determination of some inorganic ions. Some interesting examples are: titration of sulphate ions, volumetric determination of lithium and beryllium.

The composition of the book is consistent in spite of the fact that it deals with the development of several branches of chemical analysis sometimes rather remote from one another.

After a short theoretical introduction and a survey of the literature, the authors deal with the properties, purification, and in many cases also the preparation of the suggested reagents in detail, and give exact prescriptions of the analytical procedures including the elimination of interference from foreign ions. References given at the end of each part facilitate the looking up of literary data.

R. Belcher and C. L. Wilson, with the sense of scientist and practical analyst, have chosen of new analytical methods those which can be used for resolving special problems and which seem to be lasting.

The presented methods demonstrate that it is possible and necessary to produce new methods in the field of classical chemical analysis also.

The make-up of the book is nice. The good typographic work makes the book easy to read and survey.

É. Bányai

Bodie E. Douglas and Darl H. McDaniel: *Concepts and Models of Inorganic Chemistry*, Blaisdell Publishing Company, New York, 1965. XVIII + 510 pages, $ 10.50.

For a long time inorganic chemistry used to be one of the dullest subjects of the curriculum. It was a mere collection of mostly uncorrelated data. About the early forties highly efficient new tools, the development of the theory of chemical bonding, and last but not least, new practical demands resulted in an explosionlike development of this branch of science, and now it is justified to speak of the renaissance of inorganic chemistry. After an evident delay, this changed situation has come to be reflected in recent textbooks. In the last six years a dozen textbooks on "advanced" and "physical" inorganic chemistry have been published. The book under review is a remarkable addition to this series.

As the titles of chapters indicate, this volume does cover the whole field, but after presenting the fundamental principles and concepts, it treats the chemistry of the most important types of compounds:

(I) Atomic structure and the periodic table; (II) Covalent substances; (III) Ionic substances; (IV) Thermodynamic considerations; (V) The hydrogen bond; (VI) Acids and bases; (VII) The halogens; (VIII) Electron deficient compounds; (IX) Metals; (X) Coordination compounds, I. Structure and bonding; (XI) Coordination compounds, II. Stability and reaction mechanism; (XII) Experimental methods for the elucidation of the structure and bonding of chemical compounds. In the five appendices, physical constants are tabulated, the principles of nomenclature are treated, and symmetry problems outlined.

The choice of the material is excellent. The arrangement is logical, the presentation very lucid. (There is only a minor critical remark in this respect: it would have been more logical to treat the mechanism of redox reactions in Chapter XI instead of Chapter IV.) The up-to-date references instruct the students to get further information. At the end of each chapter there is a number of well chosen questions.

The typography is excellent, the text is almost free of misprints.

The book is warmly recommended as a basis for courses on advanced inorganic chemistry.

M. T. Beck

Standardmethoden der praktischen Chemie. Herausgegeben von Ernst Poulsen Nautrup unter Mitwirkung von mehreren Fachgenossen. Präparative Methoden der organischen Chemie, Lieferung 1b und 1c, Allgemeine Arbeitstechnik II und III, bearbeitet von Jürgen Gömann, Dieter Hoppe, Ernst Poulsen Nautrup. Verlag Friedr. Vieweg und Sohn, Braunschweig, 1966.

Nach einer ziemlich langen Pause sind jetzt wiederum zwei neue Lieferungen der »Präparativen Methoden« erschienen. Es sind dies die beiden, die Behandlung der allgemeinen Arbeitsmethoden abschliessenden Lieferungen 1b und 1c, und mit diesen zusammen liegen nunmehr insgesamt neun der geplanten sechzehn (ursprünglich waren es nur dreizehn) Lieferungen vor.

Auch diesmal erfolgte die Herausgabe in der bereits bewährten Lose-Blatt-Form. Stil, Einteilung, Druck, Ausstattung entsprechen dem bereits gewohnten hohen Standard der früheren Lieferungen, sodaß es genügt, wenn hier nur kurz auf den Inhalt der neuesten Lieferungen eingegangen wird.

Die »Allgemeine Arbeitstechnik. II.« schließt zuerst das Kapitel über »Das Arbeiten mit Gase« ab, bringt weiterhin ein Kapitel über die verschiedensten Arten der Filtration (normale, Saug- und Druck-, Heiß- und Kaltfiltration) und die dazu verwendeten Medien, sechs Lose-Blätter über verschiedene Arten der Destillation, wobei u. a. auch die Temperaturabhängigkeit des Dampfdruckes (Nomogramm-Beilage !), sowie die Möglichkeiten zum Erzeugen und Messen von Unterdruck behandelt werden. Hier wäre zu bemerken, daß die angegebenen klassischen Destillationsanlagen mit schräg gestelltem Liebigschem Kühler zu platzbeanspruchend sind und — wenigstens im Lande des Rezensenten — kaum mehr verwendet werden. Die in den Abb. 1 und 2 des Lose-Blattes über »Einfache Destillation unter Normaldruck

(Dampftemperaturen 50 °C)« haben sich in dieser Beziehung viel besser bewährt und können, unter Ausschluß des Leitungswassers, auch für die Destillation höher siedender Flüssigkeiten verwendet werden. Eine diesbezügliche Korrektion in einer folgenden Auflage erscheint dem Rezensenten als wünschenswert. Als Abschluß folgen je ein Kapitel über Extraktion (6 Seiten) und Aussalzen (2 Seiten).

Die »Allgemeine Arbeitstechnik. III« behandelt die Adsorption (Entfärbung mit Kohle und Säulenchromatographie, 1 bzw. 4 1/2 Seiten — ist letzteres nicht zu wenig?), die Umkristallisation, die Kolonnendestillation (zwei Teile, insgesamt 9 Seiten, wobei im zweiten Teil auch die Bestimmung der Kenngrößen einer Kolonne beschrieben wird), die Dialyse, die Trocknung von Feststoffen und Flüssigkeiten (drei Teile, insgesamt 16 Seiten, wovon der letzte Teil, die Wasserentfernung aus Lösungsmitteln mehr als die Hälfte ausmacht), die Bestimmung des Schmelz- und Siedepunktes (leider wird der Koflersche Heiztisch nur in einer Fußnote eben noch erwähnt!) und schließt endlich mit zwei Kapiteln über Reinheitsprüfungen, darunter die chromatographischen und optischen Methoden.

Trotz einiger (weniger) Meinungsverschiedenheiten des Rezensenten mit den Herausgebern möchte er Chemiestudenten und Laboranten die Anschaffung auch der neuen Lieferungen empfehlen.

K. LEMPERT

AUGUST KEKULÉ: *Cassirte Kapitel aus der Abhandlung: Über die Carboxytartronsäure und die Constitution des Benzols.* Verlag Chemie, Weinheim, 1965

Was soll der Rezensent machen, wenn er über ein Werk zu schreiben hat, dessen Verfasser AUGUST KEKULÉ heißt, das im Jahre 1883 geschrieben wurde und achtzig Jahre später, 1965, zuerst im Druck erschien? Es handelt sich um zwei Kapitel der Abhandlung KEKULÉS »Über die Carboxytartronsäure und die Konstitution des Benzols«, die in Liebigs Annalen 221, 230 (1883) erschienen ist. Diese zwei ersten Kapitel, mit den die Titeln »Die typischen Benzolformeln« und »Zur Geschichte der Valenztheorie«, sind jedoch damals nicht erschienen, weil der damalige Redakteur der Annalen, VOLHARD, KEKULÉ von der Veröffentlichung abgeraten hatte. In diesen zwei Kapiteln diskutiert KEKULÉ mit KOLBE und anderen einerseits über seinen Benzolring, den KOLBE nicht anerkennen wollte, und verteidigte andererseits seinen Anspruch auf Priorität in Hinsicht auf die Valenzlehre gegenüber KOLBE und FRANKLAND. Der Leser verfolgt Diskussionen, die heute längst entschieden sind. Die Geschichte anerkennt, daß der Hauptteil des Verdienstes and der Valenzlehre KEKULÉ gebührt, zollt jedoch auch FRANKLAND Achtung als einem der wichtigsten Vorarbeiter dieses Begriffs. Mag sein, daß KEKULÉ — wie er selbst schreibt — persönlich keine Beeinflussung durch FRANKLAND spürte, unbewußt wurde er jedoch sicher durch all die Ideen beeinflußt, die damals in der chemischen Athmosphäre schwebten.

Der Leser ist etwas überrascht, zu erfahren, daß 18 Jahre nach der Veröffentlichung der Benzolformel durch KEKULÉ darüber zu diskutieren noch nötig war. Nicht nur mit dem verbissenen KOLBE, sondern auch mit anderen Chemikern von Rang, wie z. B. mit MENDELEJEV. So langsam dringen also neue Ansichten durch! RICHARD KUHN schreibt eben deshalb sehr geistreich in der kurzen Einleitung, daß diese Ausgabe »Ein Trostbüchlein für alle, die mit neuen Ideen nicht gleich allgemeine Anerkennung finden oder deren Manuskripte von einer Redaktion gekürzt werden« ist. Dem heutigen Leser, der in einem Zeitalter lebt, in dem die Naturwissenschaftler sich fast nur mehr gegenseitig Komplimente sagen und fast nie Diskussionen miteinander führen, fällt auch der scharfe und ironische Ton auf, mit dem KEKULÉ seine Rechte verteidigte. Wer sich aber ein wenig in die Literatur des vorigen Jahrhunderts vertieft, besonders aber das »Journal für praktische Chemie« durchblättert, der wird KEKULÉ höflich und sanft nennen.

Das ist ja ganz unglaublich, was HERMANN KOLBE, dieser Starrkopf, übrigens Chemiker von Rang, aber, damals schon zur alten Generation gehörend, darin trieb! KOLBE, zu allem Unglück allmächtiger Redakteur obengenannter Zeitschrift, mußte ja damals ein wahrhaftiger Schrecken der deutschen Chemiker gewesen sein! Streitsüchtig, wie er war und sehr voreingenommen, griff er jeden an, der ihm nicht gefiel. Und am wenigsten gefiel ihm KEKULÉ und seine »verderbliche« Chemie mit dem Benzolring, den Kohlenstoffketten und Strukturformeln. Jahr für Jahr, zwei Jahrzehnte hindurch, griff er KEKULÉ wegen aller möglichen Ursachen an, es gibt kaum einen Band der Zeitschrift, in dem kein wütender Artikel dieser Art zu finden wäre. Ich zitiere nur einige:

». . . . Ich habe bei dieser Gelegenheit zum ersten Male Veranlassung gehabt, KEKULÉS Lehrbuch . . . . zu lesen. Bis dahin hatte ich, weil ich erkannte, daß ich nichts Nützliches daraus lernen konnte, dasselbe bloß flüchtig durchblättert. Ich bin erschrocken, zu sehen, wie planlos, undurchdacht und bis zur Unverständlichkeit schlecht stylisiert dieses Buch geschrieben ist, wie sehr es dem Verfasser an chemischer Einsicht gebricht und wie derselbe in Entstellung der Wahreit bis zur Fälschung derselben Unglaubliches geleistet hat . . .«

»KEKULÉ übt auf die junge Generation den allerverderblichsten Einfluß«.

»Wie diese, so sind alle Abhandlungen KEKULÉs überreich an undurchdachten Worten, Phrasen . . . und arm an brauchbaren Gedanken.«

»KEKULÉ trägt die Hauptschuld an der heutigen Verwilderung .... in der Chemie, welche wie ein Krebsschaden . . . um sich frißt«, usw.

Man lächelte gewiß über Kolbe, aber einmal vergeht doch die Geduld. So setzte sich KEKULÉ hin, um zu antworten . . . Aber VOLHARD riet ihm:

»Ein AUG. KEKULÉ hat es doch nicht nöthig des eigenen Verdienstes Künder zu werden u. kann getrost der Mit- u. Nachwelt überlassen seine u. anderer Leistungen gegeneinander abzuwägen.« KEKULÉ befolgte VOLHARDS Rat und strich zwei Kapitel. Das war auch das klügste Verhalten gegenüber KOLBE. Dieser ärgerte sich:

»Es ist bequem — schreib er empört — wenn man angegriffen wird und auf den Angriff nichts zu antworten weiß, sich in dünkelhaftes Schweigen zu hüllen und eine affectierte Vornehmheit dem wissenschaftlichen Gegner zu insinuieren . . .« Es ist interessant, dieses längst-posthumus Buch von KEKULÉ zu lesen. Der Verlag erwies der Chemiegeschichte wertvolle Dienste, indem er diese Handschrift allgemein zugänglich machte. Wirklich genießen kann es heute jedoch nur jemand, der ein wenig mit der Chemie und den Chemikern des vorigen Jahrhunderts bekannt ist. Eine längere erklärende Einleitung über die damalige Situation zuzusetzen wäre gewiß nützlich gewesen und hätte zum besseren Verständnis beigetragen. Dagegen hätte der komplette Abdruck der Original-Handschrift KEKULÉS wegbleiben können. Einige Seiten, um seine Handschrift zu zeigen, hätten meiner Meinung nach genügt; die ersten z. B., wo eben die verschiedenen Benzolformeln dargestellt sind. Dann wäre vielleicht auch das Format des Buches etwas kleiner ausgefallen und man könnte es leichter in den Bücherschrank einreihen.

F. SZABADVÁRY

G. P. ELLIS: *Modern Textbook of Organic Chemistry.* Butterworths and Co. (Publishers) Ltd., London, 1966; XII + 466 pages

According to the Preface, G. P. ELLIS' Textbook of Organic Chemistry was written as a manual for the use of such university students who have already studied organic chemistry for 1 to 2 years, have acquired therefore some experience in the rudiments of organic chemistry, and relying on these foundations, attend a modern course of organic chemistry.

The textbook is divided into 17 chapters, the first few of which discuss some fundamental notions (types of bonds and reactions, reaction mechanism, activation energy, light absorption of organic compounds, *etc.*), the next four classify the fundamental hydrocarbons according to their skeleton (alkanes and cycloalkanes, alkynes, benzenoid hydrocarbons). Thus, in accordance with a practice becoming more and more general, ELLIS does not preserve the classical division of organic chemistry into aliphatic and aromatic compounds either. The remaining chapters discuss the principal groups of compounds according to their functional groups, in agreement with the former as regards the grouping, irrespective of the differences of the carbonic skeleton. Separate chapters are dedicated to stereochemistry, chemistry of peptides and proteins, carbohydrates and heterocyclic compounds.

It is remarkable that the chapter entitled Stereochemistry dicussed merely the cis-trans and optical isomerism systematically and the other aspects of stereochemistry are treated elsewhere, *e.g.* conformational analysis in the course of the discussion of the cycloalkanes.

In the majority of the chapters the material is divided into the following sections: introduction (general characterization of the respective group of compounds, accentuation of its practical aspects), nomenclature, electronic and steric structure, reactivity, modes of preparation (indication-like recapitulation, reference to the reactions of the starting materials used for the purpose in question; this method enables to avoid repetitions and provides considerable economy of space), the more important representatives, exercises (their solution to be found at the end of volume). In the course of discussing the individual groups of compounds the author is also alluding shortly to their characteristic infrared and ultraviolet spectroscopic properties and the infrared spectrum of some characteristic representative is often given. As a useful initiative, this is definitely commendable. It is remarkable, however, that nothing is presented about nuclear magnetic resonance spectra.

In the opinion of the reviewer G. P. ELLIS' textbook is somehow not profound enough, at any rate less so than customary in textbooks that are written for advanced students. As typical instances which evoked opinion the chapters dealing with amino acids, peptides and the di- and polysaccharides can be cited.

Since it is a textbook we are concerned with some not quite clear wordings, defective concept-buildings and misprints are of special consequence. In G.P. ELLIS' book, unfortunately, quite a number of these occur. Here are some instances.

The electron formula of ethylene on p. 6 is not clear. The marking by a dot of the simple bonds (p. 6) is confusing, especially when partial electronic formulae occur in some of the equations and the dot means now an electron and now a bond, *i.e.* an electron pair, *e.g.* on pp. 16 and 18 in conjunction with the mechanism of the description of the HOFFMAN degradation and benzoil peroxyde decomposition, respectively. The definition of the $+$ I-effect (p. 10) is misleading: for the point in question here is not whether some substituent attracts or repells electrons — as stated by the author — but whether it does this more or less so than hydrogen. False ideas might follow also from the statement connected with the contrasting of the notions of resonance and tautomerism (p. 14) according to which isomers being in tautomeric relation are separable from each other. (Here the term "often" or some similar restriction is wanting).

Following p. 33 the student might form the incorrect view that the eclipsed conformation of butane is identical with the *cis* and the staggered to the *trans* conformation, although both the *cis* and the *trans* conformations are but one of the eclipsed and staggered conformations, respectively.

The statement (pp. 41—42 and 109), according to which the iodination of hydrocarbons should be performed in the presence of an oxidizing agent to the reducing hydrogen iodide formed as a by-product, is erroneous, because the iodinated product can be reduced by hydrogen iodide only under much more drastic circumstances! The role of the oxidizing agent is to transform the iodine into an iodinating agent of enhanced activity.

In the course of discussing the theory of the addition of hydrochloric acid to propylene (p. 54) there is the statement that it is secondary carbonium ion that is the more stable and also that it is formed more rapidly. The latter fact, however, does not follow from the greater stability of the ion but only from the greater stability of the respective transition state — of this, however, no mention is made.

Formulae E and F on p. 66 are two limiting structures of the same carbonium ion. Yet it is stated here that both ions may be formed: under mild conditions it is E that may be expected to be the most rapidly formed intermediate, while at elevated temperatures the energy needed for the formation of carbonium ion F (carbon ion in the original!) is also available; a severe confusion of isomerism and resonance!

Contrary to the statement at the bottom of p. 92, the numbering of the phenantrene skeleton is *not* in accordance with the general rules of numbering polycyclic hydrocarbons.

The definition of f_0 on p. 102 is incorrect. Correctly it runs as follows: f_0 = *rate of nitration of one o-position of methoxy benzene* rate of nitration *at one carbon atom* of benzene.

The statement that all halogen atoms of the polyhalogenides can be utilized in FRIEDEL—CRAFTS reactions (p. 113) is false; CCl *e.g.* is an exception.

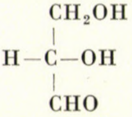
The correlation of the order and molecularity of the S_N reactions on p. 128 is oversimplified — so much so that in this form it is not true any more.

The key intermediate of the BUCHERER reactions (p. 186) — as already known from RIECHE's investigations — is *not* of the ketone-bi-sulphite type. On the other hand, the transformation of 2-naphtylamine into 2-naphthol is not effected by the action of sulphuric acid (last equation but one of p. 185) but by that of sodium bisulphite. On p. 189 it is to be read that there exist no oxygen analogues of disulphides. What about peroxides?

In the legend to Fig. 9.1 (p. 205) the C=C bonds of benzene are mentioned; these however, occur only in the fictitious limiting structures!

Another erroneous statement is one according to which the 1,2-quinones are generally suffering benylic acid rearrangement under the action of alkali (p. 237); although this reaction occurs with phenantrene quinone, it does not occur with *e. g.* by *o*-benzoquinone.

The formula in the middle of p. 259 for the definition of the D-configuration is faulty (because incomplete);



$$\begin{array}{c} CH_2OH \\ | \\ H-C-OH \\ | \\ CHO \end{array}$$

e.g. represents L-glycerine aldehyde. From the definition given by the author the requirement is, namely, missing that the carbon atom at the higher degree of oxidation ought to be put "above" and that at a lower degree of oxidation "below" if the OH group put on the right side is to indicate the D-configuration.

On p. 267 it is stated that in sulphonium salts the four valencies of sulphur (three of them covalent and one electrovalent) are arranged tetrahedrally. Instead of speaking the direction of the electrovalency it would have been more suitable to speak here of the orientation of the unshared electron pair of the central atom.

The statement that primary and secondary nitroalkanes are isomerized into the aci-form in an alkaline medium this form being a resonance hybrid (p. 335) is again incorrect. Under the action of alkali a proton is cleaved, and an anion is formed — this, in fact, being of mesomeric nature — and only on acidification is the aci-form formed in some particular cases.

On p. 341 the formula of the nitronic acid is wrong; it contains pentavalent nitrogen. Neither is the formula of the methyldiazonium cation correct (p. 355).

In the SANDMEYER reaction — according to p. 358 — the diazonium group is displaced by nucleophiles, *e.g.* halides, cyanide, nitronium (!?) or hydroxyl ions. However, it is a matter of common knowledge that the proper SANDMEYER reactions are not S_N but S_R reactions — the author himself explains it later on.

Although the mechanism of osazone formation is not yet cleared up in every detail it is quite certain that the mechanism presented on p. 389 is not correct for, according to isotopic tests, C-1 can neither take up nor lose hydrogen, not even temporarily.

On p. 397 it would not have been amiss to call attention to the fact that in reality it is not D-glucose the ring size of which is furnished by the chemical method presented, but its methyl glycoside. The formula of Vitamin B_1 on p. 405 is incomplete. On p. 409 the author speaks about the character of the C_1—C_2 bond in thiophene — but, according to its generally accepted numbering, thiophene does not contain such a bond. On p. 411 the formula of indoline is incorrect.

According to the author, the reason for the difference between the chemical properties of pyridine, *etc.* and of pyrrole, *etc.* (p. 414) is the fact that in the former the nitrogen is bound by a double bond. This, again, is only true for the limiting structures, but in this sense it is equally true for pyrrole. It is therefore evident that the explanation given is erroneous.

On p. 420 the "presence" of certain resonance forms of pyridine-N-oxide is mentioned although obviously, these represent only nonexistent, fictitious linufuy structures. Some lines further the reactivity of pyridine-N-oxide, anol the orientation phenomena observed on this compound, are attributed to the charge distribution of the non-reacting molecule. This is to say the least an extremely one-sided treatment.

The reviewer believes that, having listed such a number of objections, he has motivated sufficiently why it would be difficult for him to recommend the acquisition of P. G. ELLIS' book to his students.

K. LEMPERT

The Chemistry of the Carbonyl Group. Edited by SAUL PATAI, The Hebrew University, Israel. Interscience Publishers, John Wiley and Sons. Inc. 605 Third Ave., New York, N. Y. 1966. XII + 1027 pp.

The book edited by Prof. PATAI as the second volume of a series on functional groups in organic compounds deals with chemistry of carbonyl groups. The first of the 17 chapters of the book of more than 1000 pages is concerned with the physical chemistry, the next five with chemical methods of preparation, the 8th with the physical and chemical methods of determination, and the next chapter with the basicity of carbonyl compounds. Six chapters are devoted to chemical reactions, and in three separate chapters some special topics are treated in connection with the subject.

Chapter 1 ("General and theoretical aspects of the carbonyl groups" by G. BERTHIER and J. SERRE) is concerned with the physicochemical properties of the carbonyl group such as physical characteristics, IR and UV spectra; the second subdivision on the quantum-chemical interpretation of the carbonyl group utilizes the excellent compilation written by COULSON and STEWART in the first book of the series. Chapter 2 ("Carbonyl forming oxidations" by C. F. CULLIS and A. FISH) treats the oxidation of alkanes and cycloalkanes, alkenes, cycloalkenes, alkynes, and aromatic hydrocarbons, carried out with molecular oxygen and specific oxidizing agents. Chapter 3 ("Formation of carbonyl groups in hydrolytic reactions" by **Pentti Salomaa**) describes reactions in which the hydrolysis of disubstituted saturated compounds (*e. g.* α,α'-dihalides), or certain unsatured compounds (*e. g.*, imines) results in the formation of carbonyl groups. Chapter 4 ("Formation of aldehydes and ketones from carboxylic acids and their derivatives" by **R. C. Fuson**) deals with the pyrolysis of acids, their salts and anhydrides, and also with the hydrogenolysis of acid derivatives. Chapter 5 ("Formation of ketones and aldehydes by acylation, formylation and some related processes" by **D. P. N.** and **R. S. Satchell**) is devoted to methods involving direct introduction of carbonyl groups and formation of new carbon-carbon bonds. Chapter 6 ("Carbonyl syntheses through organometallics" by **M. Cais** and **A. Mandelbaum**) gives a survey of organometallics that have beeen used to prepare carbonyl groups for nearly a hundred years.

The subject of Chapter 8 is the analytical chemistry of compounds containing carbonyl groups ("Chemical and physical methods of analysis" by **J. Gordon Hanna**); it offers a thorough survey of new physical methods in addition to a discussion of chemical methods which may now be considered classical. In Chapter 9 ("Basicity of carbonyl compounds" by **V. A. Palm, Ü. L. Halina** and **A. J. Talvik**) the basicity of carbonyl compounds, a difficult problem is considered including the definition of basicity. The next six chapters deal with the reactions of carbonyl groups, such as the oxidation of aldehydes with compounds of chromium, manganese, vanadium, cerium and cobalt ("Oxidation of aldehydes by transition metals" by **J. Roček**); reduction methods leading to various compounds ("Reduction of carbonyl groups" by **O. H. Wheeler**); condensation reactions resulting in the formation of new carbon-carbon and carbon-nitrogen double bonds ("Condensations leading to double bonds by **R. L. Reeves**); reactions with organometallics ("Reactions of carbonyl groups with organometallic compounds" by **T. Eicher**), with special emphasis on reaction mechanisms; decarbonylation reactions ("Decarbonylation" by **W. M. Schubert** and **R. R. Kintner**), including the ones in which the formyl groups of aldehydes transform into formic acid or formate ion; thermal, oxidative and photochemical rearrangements and those catalyzed by acids or bases (("Rearrangements involving the carbonyl group" by **C. J. Collins** and **J. F. Eastham**). Chapters 7, 16 and 17 treat special topics including the biological and photochemical aspects of the field ("Biological formation and reactions of carbonyl groups" by **F. Eisenberg**, Jr.; "Photochemistry of ketones and aldehydes" by **J. N. Pitts**, Jr. and **J. K. S. Wan**; and "Thioketones" by **E. Campaigne**).

The book, in accordance with the purpose of the series, avoids encyclopedic treatment, its purpose being, as stated in the foreword "to encompass all facets of a functional group and to give up-to-date descriptions of the nature of the carbonyl group". The authors of the different chapters, essentially of independent monographs, only refer to questions dealt with in modern handbooks or in summaries, and put the emphasis on presenting new results.

The value of the excellently edited and nicely got up book is increased by a list of references at the end of each chapter, altogether adding up to more than 3000 references. This very interesting book affords valuable help to organic chemists and those taking an interest in recent developments of organic chemistry. The book arouses interest in the subsequent volumes of the series.

Gy. Deák

Márta Déri: *Ferroelectric Ceramics*. Akadémiai Kiadó (Publishing House of the Hungarian Academy of Sciences) Budapest, 1966. 94 pp.

The Hungarian version of the book was published in 1963 by the same publisher, as Volume 5 of the series "*Monographs of Silicate Chemistry*".

In the English translation now reviewed, after a short introduction, the present state of researches and achievements in the field of ferroelectric ceramics is discussed in six chapters on 81 pages. This is completed by a description of developments attained in Hungary since 1945, the major part of which are the results of the author. The text is illustrated by 54 figures and 6 tables; the book contains a bibliography, a list of authors cited, and subject index.

The author wrote her book mainly for experts in silicate chemistry and ceramics, thus the principal subject is a discussion of polycrystalline ferroelectrics. A treatment of problems of interest for theoretical physicists would have been outside the scope of the present monograph.

In Chapter I (pp. 1—7) the definition of ferroelectricity and a description of related properties are given. The chapter is completed by a phenological systematization which serves as a basis for the further discussions.

In Chapter II (pp. 8 to 27) ferroelectrics of perovskite structure are described, summarizing the structural conditions and physical properties, important from the point of view of ceramics, of single crystal barium-titanium trioxide and of polycrystalline barium titanate. The chapter gives then a survey of the theories concerning the interpretation of ferroelectricity.

Chapter III (pp. 28 to 31) deals with the structure of ferroelectrics of the pyrochlore type, with the physical properties of single crystals belonging to this class, and with polycrystalline substances prepared by ceramic methods.

In Chapter IV (pp. 32 to 35), ferroelectrics of the niobate type are surveyed, and their structural and physical properties described. The chapter is concluded with a table showing the ferroelectric groups of importance from the aspect of ceramics.

Chapter V (pp. 36 to 78) is devoted to the discussion of ferroelectric solid solutions, mixed crystalls and polycrystalline substances. This chapter, the longest one in the book, is divided into subchapters which deal in detail with various materials possessing ferroelectric and related properties, with the modes of suppressing ferroelectric phase transition, and with the possibilities of multiple ion substitutions. In the last paragraphs of this chapter, the author shortly describes ferroelectrics of perovskite structure having semiconducting properties.

Chapter VI (pp. 79 to 81) deals with the problems of application and development of ferroelectric ceramics. This question is approached in two ways. First, the potential fields of application are described on basis of the given crystallographic and physical properties; secondly, possibilities in ceramic technology are surveyed to develop the desired properties of the products.

The interesting book of M. DÉRI discusses the theoretical fundamentals of a new branch of industry operating according to the technological processes of the classic ceramic industry. As suggested by VERWEY, this branch may be denoted as synthetic ceramic industry. Ferroelectric ceramics of this type are indispensable in the telecommunication industry and in low-voltage electric operations, such as the manufacture of capacitors of small dimensions, dielectric amplifiers, *etc.* The various constituents of computers operating in the numerical system 2, ultrasonic vibration elements, pick-up devices, *etc.*, are today prepared with the application of ferroelectrics to a large extent.

It is pointed out that the ferroelectric systems discussed in the book are far from comprising all published data; they serve rather as characteristic examples for the principal types. Many problems mentioned in the book are unsolved, and will probably remain so for some time, owing to the novelty and complex nature of the field.

The book can be sincerely recommended to those working in silicate chemistry and mainly in the ceramic industry, since the theoretical background of the field is summarized in a systematic form. After studying the work of M. DÉRI, it will be easier for practical ceramic chemists to approach and solve problems of industrial development.

Lucid presentation of the subject-matter and a logical systematization in M. DÉRI's book will contribute to a great extent to the development of this modern and new branch of ceramic industry based on an integration of theoretical and practical knowledge.

The English version of the work reviewed above has been published in a representatively nice form, in joint edition with *Maclaren and Sons, Ltd.*, London.

Mrs. R. MOLDVAI

Printed in Hungary

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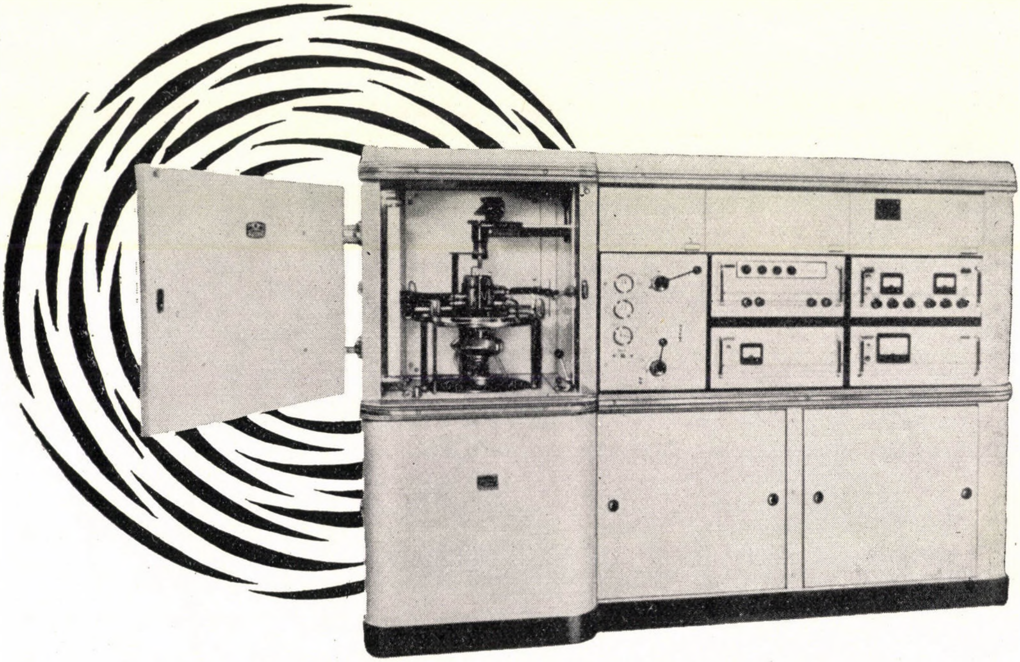

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